3

Corresponding to

US 5527876

(19)日本国特許庁（ＪＰ）　(12) 特　許　公　報（Ｂ２）　(11)特許番号 特許第3309980号 (P3309980)

(45)発行日　平成14年7月29日(2002.7.29)　(24)登録日　平成14年5月24日(2002.5.24)

(51)Int.Cl.7	識別記号	ＦＩ	
ＣＯ８Ｇ　18/34		ＣＯ８Ｇ　18/34	Ｆ
			Ｚ
18/20		18/20	
ＣＯ８Ｊ　5/18	ＣＦＧ	ＣＯ８Ｊ　5/18	ＣＦＧ
ＣＯ９Ｄ 177/00		ＣＯ９Ｄ 177/00	

請求項の数29(全 22 頁)　最終頁に続く

(21)出願番号　特願平5－512917

(86)(22)出願日　平成5年1月22日(1993.1.22)

(65)公表番号　特表平7－503037

(43)公表日　平成7年3月30日(1995.3.30)

(86)国際出願番号　ＰＣＴ／ＥＰ９３／００１４５

(87)国際公開番号　ＷＯ９３／１５１２１

(87)国際公開日　平成5年8月5日(1993.8.5)

審査請求日　平成12年1月17日(2000.1.17)

(31)優先権主張番号　Ｐ４２０２７５８．６

(32)優先日　平成4年1月31日(1992.1.31)

(33)優先権主張国　ドイツ（ＤＥ）

(31)優先権主張番号　Ｐ４２１５６４７．５

(32)優先日　平成4年5月13日(1992.5.13)

(33)優先権主張国　ドイツ（ＤＥ）

(73)特許権者　999999999
ヘンケル・コマンディットゲゼルシャフト・アウフ・アクチェン
ドイツ連邦共和国　デー－40191　デュッセルドルフ　（番地の表示なし）

(72)発明者　クルート、ヘルマン
ドイツ連邦共和国　デー－4000　デュッセルドルフ　1、デーガーシュトラアセ48番

(72)発明者　ダウテ、ペーター
ドイツ連邦共和国　デー－4300　エッセン　1、クロイツェス－キルヒシュトラアセ　5番

(74)代理人　999999999
弁理士　青山　葆　（外2名）

審査官　佐藤　健史

最終頁に続く

(54)【発明の名称】アミド基を有するプラスチックの製造方法

(57)【特許請求の範囲】

【請求項１】Ａ）多官能性の脂肪族、脂環式または芳香族イソシアネートおよび／またはそれらから製造したNCO末端のオリゴマー化した生成物を、

Ｂ）カルボン酸、および場合により

Ｃ）アルコールまたは多官能性の１級または２級アミンと、

（少なくともＢ）またはＣ）は多官能性でなければならず、および／またはＢ）およびＣ）は合わされてヒドロキシカルボン酸またはアミノカルボン酸を形成する。）100℃未満の温度で触媒としての３級アミンの存在下で、CO_2を脱離して触媒的に反応させることによるアミド基を有する熱可塑性材料または熱硬化性材料の製造方法であって、

３級アミンとしてアミノ置換ピリジンおよび／またはＮ－置換イミダゾールを用いる方法。

【請求項２】反応物の混合の間または出発混合物の加熱の間、温度を50℃未満とすることを特徴とする請求の範囲第１項に記載の方法。

【請求項３】反応時間を、反応物の混合から実質的に完全な硬化まで24時間未満とすることを特徴とする請求の範囲第１または２項に記載の方法。

【請求項４】カルボン酸が少なくとも２個の炭素原子を有することを特徴とする請求の範囲第１～３項のいずれかに記載の方法。

【請求項５】ヒドロキシカルボン酸が２～600個の炭素原子を有することを特徴とする請求の範囲第１～４項のいずれかに記載の方法。

【請求項６】ポリヒドロキシカルボン酸が、エポキシ化した不飽和脂肪酸エステルの、ヒドロキシ官能性の化合

物による開環反応、および場合によりその後のケン化により得られることを特徴とする請求の範囲第５項に記載の方法。
【請求項７】開環に用いるジオールが、エタン－1,2－ジオール、ブタン－1,2－ジオール、ヘキサン－1,6－ジオール、２～40の重合度を有するポリプロピレングリコール、ポリブタジエンジオールおよび／またはポリエチレングリコールであることを特徴とする請求の範囲第６項に記載の方法。
【請求項８】エポキシ化した不飽和脂肪酸または脂肪酸混合物が８～100個の炭素原子の鎖長を有することを特徴とする請求の範囲第６項または第７項に記載の方法。
【請求項９】芳香族の多官能性イソシアネートおよび／またはNCO末端のオリゴマー化した合成生成物により特徴づけられる請求の範囲第１～８項のいずれかに記載の方法。
【請求項１０】イソシアネートがカルボン酸とのみ反応する場合には、１当量のイソシアネートに対して0.1～４当量のカルボン酸および0.001～0.1当量の３級アミンを用いることを特徴とする請求の範囲第１～９項のいずれかに記載の方法。
【請求項１１】イソシアネートがカルボン酸およびアルコールと反応する場合には１当量のイソシアネートに対して0.1～２当量のカルボン酸およびアルコールの混合物または１級もしくは２級アミンまたはアミノアルコール、および0.001～0.1当量の３級アミン、または３級アミンがNCO反応性の基を含む場合には２当量までの３級アミンを用い、カルボン酸とアルコールの比は1:20～20:1であることを特徴とする請求の範囲第１～９項のいずれかに記載の方法。
【請求項１２】イソシアネートがアミノ－またはヒドロキシカルボン酸と反応する場合には、イソシアネート基と活性水素を有する基との当量比は2:1～0.5:1であることを特徴とする請求の範囲第１～９項のいずれかに記載の方法。
【請求項１３】イソシアネート、カルボン酸および３級アミンおよび／またはヒドロキシカルボン酸またはアミノカルボン酸、および場合によりアルコールおよび多官能性アミンを同時に一緒にし、次に完全開放型中またはベルト上で加工して、スラブまたはサンドイッチ要素を形成することを特徴とする請求の範囲第１～12項のいずれかに記載の方法。
【請求項１４】成分を素早く計量し、混合し、反応性の混合物を実質的にまたは完全に閉じた型の中に射出し、その中で24時間かけて硬化させることを特徴とする請求の範囲第１～12項のいずれかに記載の方法。
【請求項１５】反応混合物を、反応物の混合中100℃未満の温度とすることを特徴とする請求の範囲第１～14項のいずれかに記載の方法。
【請求項１６】酸価が40未満であることを特徴とする請求の範囲第１～15項のいずれかに記載の方法により得られるプラスチック。
【請求項１７】アミド基に加えてエステル、尿素および／またはウレタン基を有することを特徴とする請求の範囲第16項に記載のプラスチック。
【請求項１８】密度が非多孔性プラスチックの密度より多くとも25%小さいことを特徴とする請求の範囲第16項または第17項に記載のプラスチック。
【請求項１９】密度がその気泡構造（発泡体）のために、最大で800kg/m^{3}であることを特徴とする請求の範囲第16項または第17項に記載のプラスチック。
【請求項２０】使用温度で発泡する接着剤および封止剤として、請求の範囲第16～19項のいずれかに記載のプラスチックを使用する方法。
【請求項２１】２成分の構造およびアセンブリ発泡体として、請求の範囲第19項に記載のプラスチックを使用する方法。
【請求項２２】絶縁および包装のため、請求の範囲第19項に記載のプラスチックを使用する方法。
【請求項２３】フラワーアレンジメント発泡体として、請求の範囲第19項に記載のプラスチックを使用する方法。
【請求項２４】インテグラル発泡体として、請求の範囲第19項に記載のプラスチックを使用する方法。
【請求項２５】スラブ材発泡体として、請求の範囲第19項に記載のプラスチックを使用する方法。
【請求項２６】注型用コンパウンドの製造のため、請求の範囲第16～19項のいずれかに記載のプラスチックを使用する方法。
【請求項２７】コーティングのため、請求の範囲第16～19項のいずれかに記載のプラスチックを使用する方法。
【請求項２８】射出成形物品または繊維もしくはフィルムの製造のため、請求の範囲第16～19項のいずれかに記載のプラスチックを使用する方法。
【請求項２９】連続気泡発泡体およびそれから得られるフィルターの製造のため、請求の範囲第16～19項のいずれかに記載のプラスチックを使用する方法。
【発明の詳細な説明】
本発明は、CO_2の生成を伴う、カルボン酸と多官能性イソシアネートとの接触反応によるアミドを有する熱可塑性材料または熱硬化性材料の製造方法、その製造方法により得られるプラスチック、およびその使用に関する。
イソシアネートと反応した時カルボキシル基が二酸化炭素を放出し、PURプラスチックにおける発泡反応に寄与することは一般的に知られている。
かくして、オー・ベイアー（O. Bayer）（アンゲバンテ・ヘミー（Angewandte Chemie）、59巻、1947年、257～288頁参照）は、267頁に、（ａ）遊離のヒドロキシル基とカルボキシル基の両者を有する、ジカルボン酸と

三価アルコールのポリエステルと、（b）ジイソシアネートとの発泡体を記載する。50〜300kg/m^3の発泡体が得られている（商標：モルトプレン（MOLTOPREN））。工業的規模で用いる芳香族イソシアネートの場合には、このNCO/COOH反応は非常に複雑で、工業的規模の発泡反応、すなわち比較的低密度を得るには適当でない。さらに、この方法で得られるポリウレタンはしばしば強く着色する。

ドイツ特許3223567号に記載されたように、発泡剤としてギ酸を用いることにより改良がなされた。この文献によればポリウレタン発泡体がカルボン酸、ポリオール、ジイソシアネート、３級アミンおよび水から製造される。ギ酸はカルボン酸として使用する（実施例参照）。発泡剤として水を用いることは絶対的に必須ではない（６頁、11〜27行参照）。有機金属化合物の外に上述した触媒は、ジメチルベンジルアミン、テトラメチルエチレンジアミン、トリエチレンジアミン、ヘキサメチレンテトラミンおよびジメチルシクロヘキシルアミン等の３級アミンを含む。反応が起こる温度は具体的に述べられていない。

この方法の欠点は発泡ガスとしてCO_2の外にCO（非燃焼性、毒性）を発生することである。水で発泡する発泡体の場合と同様に、ギ酸を発泡直前にポリオール／イソシアネート混合物に加えねばならない。さらに、極性のギ酸は水と全く同様に大部分の他のPUR原料と相溶性がない。

ドイツ特許第3041589号は発泡プラスチック製造用の発泡剤としてのカルボン酸／カルバミン酸無水物の混合物を記載する。それらは弱いモノまたはポリカルボン酸との反応により脂肪族および／または脂環式イソシアネートから得られる。その無水物は40℃を超える融点を持つ必要がある。CO_2の発生には100℃を超える温度を必要とするが、ある場合にはCO_2の放出は実際上約60〜70℃で始まる。実際の発泡反応には触媒を必要としない。しかしながら、触媒、例えば有機金属化合物、マンニッヒ塩基、Ｎ－メチルモルホリン、1,2－ジアザビシクロー（2,2,2）－オクタン、ビス－（ジメチルアミノアルキル）－ピペラジンおよび1,2－ジメチルイミダゾール等の３級アミンを用いることが可能であり、有機金属化合物（例えば、有機スズ化合物）が好ましい。少なくとも128kg/m^3の密度を有する半硬質〜硬質のPURが得られる。高い出発温度（発泡剤を非常に使用し難くする）および発泡体の高密度は別として、問題の方法は次の欠点を伴う（ドイツ特許第3840817号、２頁参照）：

「混合した無水物は一方では約60℃までの温度での貯蔵において、溶液中においてすら安定であるべきであり、他方、二酸化炭素の脱離を伴って約80℃という低い温度でさえその発泡効果を発揮すべきである。したがって、二酸化炭素が脱離する温度に対する非常に狭い制限がある。脂肪族のイソシアネートのみを、混合無水物の製造に使用できる。対照的にポリイソシアネート成分として典型的に用いる芳香族ポリイソシアネートは特別の発泡剤の製造に適しない。

その方法を実施するためにその混合無水物を先ず別の反応で製造し、単離し、最後にポリオール混合物と注意深く混合しなければならない。これらは、これらの化合物を用いるコストを加える付加的な工程であり、それらの使用を複雑にする。上述した発泡剤を有する使用の準備のできたポリオールは安全に貯蔵し、移送することが困難である。何故なら、注意深い取り扱いにも拘わらず、時に生じ得るオーバーヒートの場合に圧力の危険な上昇の恐れを除くことができないからである。」

ドイツ特許第2607999号は、ヒドロキシ官能性の有機化合物と、過剰のポリイソシアネートとの、イソシアネート三量化触媒、発泡剤、および場合により典型的なポリウレタン触媒および他の添加剤の存在下における反応により得られる発泡体を記載する。反応混合物へ、当量のイソシアネート当たり0.001〜0.05当量のカルボン酸を加えることが特に重要であり、カルボン酸は実際の発泡剤として用いるのではなく、性質を改変するために用いる。その発明によれば、水および／または容易に揮発する有機化合物を発泡剤として用いる。重合反応に用いる触媒は、室温のような低い温度で三量化反応を開始する化合物、例えば、マンニッヒ塩基および２級アミンである。ポリウレタン反応は例えば、Ｎ－メチルモルホリン、1,4－ジアザビシクロー（2,2,2）－オクタン、Ｎ－メチル－N'－ジメチルアミノエチルピペラジンおよび1,2－ジメチルイミダゾール等の典型的な触媒の存在下に行う。この方法の欠点は水または揮発性の有機化合物を発泡剤として用いねばならないことである。かくして、トリクロロフルオロメタンをすべての実施例において用いている。

ドイツ特許第423594号は、少なくとも250kg/m^3の密度を有するポリウレタン発泡体成形物の製造方法を記載し、その目的のために芳香族ポリイソシアネートを有機のポリヒドロキシル化合物と、有機カルボン酸の少なくとも一つのＮ－Ｈ結合を有する窒素塩基との塩の存在下に反応させる。３級アミノ基を有するアミンも、N,N－ジメチル－1,3－プロピレンジアミンのように、３級アミノ基の外に少なくとも１個の１級または２級アミノ基を有するなら、用いてもよい。この方法の欠点の一つは更なる発泡剤の不存在下では半硬質〜硬質の一体の発泡体を製造することが可能なだけであるということである。

ドイツ特許第3840817号はポリウレタン発泡体成形物の製造方法およびこの方法により得られる成形物を記載し、少なくとも250kg/m^3の密度が得られる。カルボン酸を発泡剤として用いる。例えば乳酸およびその水溶液のように、カルボキシル基の外に少なくとも一つの他のイソシアネート反応性の基を有するカルボン酸が特に好ま

しい。３級アミンと有機金属化合物を触媒として用いる。この場合にも発泡体の比較的大きい密度および50℃という好ましい温度が欠点である。

イギリス特許第863,466号は、ａ）共役ジエンと６個までの炭素原子を有する脂肪族の不飽和カルボン酸との共重合体、および（ｂ）有機ポリイソシアネートよりなる発泡体の製造を記載する。水またはジカルボン酸を密度に影響を与えるために好ましくは加える。反応速度を温度により、および塩基の添加によりコントロールする。次の塩基を具体的に述べている：ジフェニルアミン、ｐ－フェニレンジアミン、ジフェニルグアニジン、グアニジン、アニリン、ベンジジン、0,0'－ジクロロベンジジン、アニシジン、アミノピリジン、2,2－ジピリジルアミン、２－アミノ－4,6－ジメチルピリジン、ヘキサメチレンテトラミン、ヒドラジン水和物、水酸化カルシウムおよび炭酸アンモニウム。実施例中反応温度は70～110℃の範囲である。反応は約１時間続く。この方法により得られる発泡体の密度に関し詳細は述べられていない。

ユニオン・カーバイト社の様々な特許明細書（例えば、米国特許第4,528,334号）は、ポリ（オキシアルキレン）へのアクリル酸のグラフト（３～15重量%）により製造されたカルボキシル化ポリオールを記載する。このタイプの生成物はウカールモンド（UCARMOND）の名前で現在市販されている。それらは約400～3,000の範囲の分子量を有する。類似の生成物はPUR分散体の製造についての欧州特許第119349号（オリン社（Olin Corporation））に記載されている。しかしながら、この場合にはマレイン酸および／またはフマル酸をグラフトのために用いる。しかしながら、その生成物は微孔性のポリウレタンエラストマーの製造にも用いる（プロシーディングス・オブ・ザ・ピー・ユー・アール・ワールド・コングレス（Proceedings of the PUR World Congress）、1991年９月、686～690頁参照）。そこに述べられた応用では、適当な反応速度を得るために、原料を33～40℃の温度に予熱し、金型は50℃の温度に加熱しなければならない。得られるエラストマーは、グラフトした酸のパーセントにより、密度が160～320kg/m^{3}で変化する。

国際出願WO91/00305号（バテレ・インスティテュート（Batelle Institute））は脂肪酸をベースにしたプラスチックに関し、ジ脂肪酸ジアミド、ジエステル、アミドエステル、モノ脂肪酸アミドジアミンまたは少なくとも２個の官能基を有するモノ脂肪酸アミドアルコールをモノマー単位として用いる。12－ヒドロキシステアリン酸およびヘキサメチレンジイソシアネートからの弾性の発泡体プラスチックの製造が実施例11に記載されている。反応は比較的高温（150℃）でのみ起こる。得られる発泡体の密度の詳細は示されていない。

ドイツ特許出願第4120432号は、ポリウレタンシステムにおける使用のための構造単位として適したジヒドロキシ脂肪酸を記載する。ポリウレタン水性分散体の製造を可能性のある応用として述べている。非芳香族のイソシアネートが好ましくは用いられ、カルボキシル基はNCO基と反応しない。

要約すると、今日までPURシステム用の発泡剤としてのカルボン酸の使用は、特に比較的高温の使用、不適当な発泡効果、大きい密度、不完全な反応、毒性で引火性のガスの生成を含む多くの欠点を伴うと言える。これらはドイツ特許第3041589号に述べられている様に工業的な利用に障害となり得る。

これらの背景に対して、本発明により取り扱われる問題は、上述した欠点がもしあったとしても非常に少ない方法を提供することである。特には、加熱しなければならない出発反応混合物を用いることなしに、プラスチック、特には多孔性の構造を有するもの（発泡体）を容易に得ることがこの方法により可能であろう。しかし、特別な場合には僅かな加熱で十分であろう。反応は工業的に受容できる時間内に実質的に完結する。

本発明により提供される解決方法は請求の範囲で特徴づけられる。それは比較的低温でのカルボン酸およびイソシアネートの反応に対するある触媒の選択に特に基づいている。生成するCO_2の脱離が強力なので、気泡生成のために用いられるフルオロカーボンおよび水などの従来の発泡剤を全く必要としない。本発明による解決方法の他の利点は、多量の、実質的に定量的な二酸化炭素生成を伴う、用いるカルボン酸のポリマー鎖への実質的に完全な導入である。

３級アミンが存在するなら室温のような低い温度でポリイソシアネートと共にあるヒドロキシカルボン酸またはカルボン酸およびポリオールから短時間に驚くほどスムーズに細かい気泡の発泡体が得られるという発見にも本発明は基づく。この気泡構造により、その密度は、選択的な触媒およびOH価および酸価のコントロールにより、25～800kg/m^3、好ましくは30～250kg/m^3、特には40～80kg/m^{3}に変えることができる。

しかしながら、高密度を有するプラスチックも、例えば反応を加圧下にまたは撹拌しながら行うことにより、安定な気泡系の生成を妨げることによって製造できる。しかしながら、この場合には非多孔性プラスチックの密度より25%以上小さい密度を有するプラスチックが得られる。

アミド基を有する熱可塑性材料または熱硬化性材料の製造のための本発明による方法は、

Ａ）多官能性の脂肪族、脂環式または芳香族イソシアネートおよび／またはそれらから製造したNCO末端のオリゴメリ化した生成物を、

Ｂ）カルボン酸、および場合により

Ｃ）アルコールまたは多官能性の１級若しくは２級アミンと

（少なくともB）またはC）は多官能性でなければならず、および／またはB）およびC）は結合してヒドロキシカルボン酸またはアミノカルボン酸を形成する。）CO_2を脱離して３級アミン存在下に接触反応させることを含んでなる。問題のタイプのアミンは知られている（エッチ・バイアー（H. Beyer）のレールブッフ・デル・オーガニッシェン・ヘミー（Lehrbuch der organischen Chemie）、18版、613頁参照）。

本発明において「プラスチック」とは、その必須成分が高分子の有機化合物よりなる物質であると理解される。もし、それらがそれらの塊全体に分布した連続および／または独立気泡を有するなら、そしてそれ故それらの密度が構造形成性のプラスチックの密度より25%以上低いなら、それらを「発泡体プラスチック」または短く「発泡体」と呼ぶ。

「カルボン酸」とは一以上のカルボキシル基（－COOH）を有する酸であると理解される。そのカルボキシル基は飽和の、不飽和のおよび／または分岐のアルキルまたはシクロアルキル基、または芳香族基に結合する。それらはエーテル、エステル、ハロゲン、アミド、アミノ、ヒドロキシおよび尿素基等の他の基を有してもよい。しかし、好ましいカルボン酸は、天然の脂肪酸または脂肪酸混合物、COOH末端のポリエステル、ポリエーテルもしくはポリアミド、ダイマー脂肪酸およびトリマー脂肪酸等の室温で液体として容易に加工できるものである。次のものが本発明によるカルボン酸の具体例である：酢酸、吉草酸、カプロン酸、カプリル酸、カプリン酸、ラウリン酸、ミリスチン酸、パルミチン酸、ステアリン酸、イソステアリン酸、イソパルミチン酸、アラキン酸、ベヘン酸、セロチン酸およびメリシン酸、およびモノ不飽和またはポリ不飽和酸、パルミトール酸、オレイン酸、エライジン酸、ペトロセリン酸、エルカ酸、リノール酸、リノレン酸、ガドレイン酸。次のカルボン酸も挙げることができる：アジピン酸、セバシン酸、イソフタル酸、テレフタル酸、トリメリト酸、フタル酸、ヘキサヒドロフタル酸、テトラクロロフタル酸、シュウ酸、ムコン酸、コハク酸、フマル酸、リシノール酸、12－ヒドロキシステアリン酸、クエン酸、酒石酸、二量化または三量化した不飽和脂肪酸（場合によりモノマー不飽和脂肪酸および所望によりこれらの化合物の部分エステルとの混合物）。TMP［$C_2H_5-C(CH_2OH_3)$］、グリセロール、ペンタエリスリトール、ソルビトール、グリコールおよびそれらのアルコキシレートとアジピン酸、セバシン酸、クエン酸、酒石酸とのエステル、ポリカルボン酸によりグラフトされまたは部分的にエステル化された炭水化物（糖、デンプン、セルロース）、およびエポキシドの開環生成物等の、COOHおよびOH基の両方を有するポリカルボン酸またはカルボン酸混合物の複合エステルを用いることも可能である。好ましいカルボン酸は少なくとも２個の、特には、５～400個の炭素原子を有する。

「ヒドロキシカルボン酸」とは２～600、好ましくは８～400、特には14～120個の炭素原子を有し、H－C基、特には脂肪族基において１～９、好ましくは２～３個のヒドロキシル基またはカルボキシル基を有する、モノヒドロキシモノカルボン酸、モノヒドロキシポリカルボン酸、ポリヒドロキシモノカルボン酸およびポリヒドロキシポリカルボン酸であると理解される。

ポリヒドロキシモノカルボン酸とポリヒドロキシポリカルボン酸は合わせてポリヒドロキシ脂肪酸を形成する。

本発明による使用に適したポリヒドロキシ脂肪酸は不飽和脂肪酸のエステルを最初にエポキシ化し、次にエポキシドを過剰の水素活性な化合物、特にａ）ヒドロキシ官能性の化合物、例えばヒドロキシカルボン酸、脂肪族ポリオールと、またはｂ）カルボキシ官能性の化合物、特には多塩基性カルボン酸と、および／またはｃ）水と反応させて開環し、場合によりエステル交換する（反応は塩基または酸により触媒される）ことにより便利に製造する。アルカリ金属水酸化物を20～60℃の温度で反応混合物に次に加え、その後、反応混合物を80～110℃でケン化し、ポリヒドロキシ脂肪酸を形成させる。ヒドロキシカルボン酸、脂肪族ポリオールおよび／または水を、エポキシ開環反応において化学量論量または化学量論量以下用いると、架橋反応も本発明においてポリヒドロキシ脂肪酸とみなされるポリヒドロキシポリ脂肪酸の形成と共に起こる。

好ましく用いるジヒドロキシ脂肪酸およびその製造はドイツ特許公開第3318596号および欧州特許第237959号に記載されている。それらは本明細書の一部を構成する。

本発明によるポリヒドロキシ脂肪酸は天然に存在する脂肪酸から好ましくは誘導する。したがって、それらは主鎖に偶数の炭素原子を一般に有し、分岐していない。C_8～C_{100}、好ましくはC_{14}～C_{22}の鎖長を有するものが特に適している。天然脂肪酸は工業用の混合物として一般的に用いる。これらの混合物は好ましくはオレイン酸成分を含有する。さらに、それらは他の飽和、モノ不飽和およびポリ不飽和脂肪酸を含有してもよい。原理的には、飽和成分または二重結合を有するポリヒドロキシアルコキシカルボン酸をも含む様々な鎖長の混合物も、本発明による使用に適するポリヒドロキシ脂肪酸またはポリヒドロキシアルコキシ脂肪酸の製造に用いてもよい。したがって、純粋なポリヒドロキシ脂肪酸のみならず、ワーキングアップ（エステル開裂、精製段階）後に40%以上、好ましくは60%以上のモノ不飽和脂肪酸含量を有する、動物脂肪または植物油から得られる混合製品もこの目的に適している。そのような混合製品の例は、例えば67%のオレイン酸、２%のステアリン酸、１%のヘプタデカン酸、10%の飽和C_{12}～C_{16}酸、12%のリノール

酸、２％の18個以上の炭素原子を有する飽和酸という鎖分布を有する牛脂、例えば約80％のオレイン酸、５％のステアリン酸、８％のリノール酸および約７％のパルミチン酸という組成を有する新しいヒマワリの油（NSf）等の商業的に入手可能な天然の原料である。これらの製品は開環後簡単に蒸留して、不飽和脂肪酸エステル成分を減らしてもよい。更なる精製工程（例えば、比較的長く続く蒸留）も可能である。

本発明によるポリヒドロキシ脂肪酸は好ましくはモノ不飽和脂肪酸から、例えば4,5－テトラデセン酸、9,10－テトラデセン酸、9,10－ペンタデセン酸、9,10－ヘキサデセン酸、9,10－ヘプタデセン酸、6,7－オクタデセン酸、9,10－オクタデセン酸、11,12－オクタデセン酸、11,12－エイコセン酸、11,12－ドコセン酸、13,14－ドコセン酸、15,16－テトラコセン酸および9,10－キシメニン酸から誘導する。オレイン酸（9,10－オクタデセン酸）が好ましい。上述したすべての脂肪酸のシスおよびトランス異性体の両方が適している。

デシル－12－エン酸、スティリンジア酸、ドデシル－９－エン酸、リシノール酸、ペトロセリン酸、バクセン酸、エレオステアリン酸、プニカ酸、リカン酸、パリナリン酸、ガドレイン酸、アラキドン酸、５－エイコセン酸、５－ドコセン酸、セトレイン酸、5,13－ドコサジエン酸および／またはネルボン酸等の一般的に生じ難い不飽和脂肪酸から誘導されるポリヒドロキシ脂肪酸も適している。

天然の不飽和脂肪酸の異性化生成物から製造されるポリヒドロキシ脂肪酸も適している。この方法で製造したポリヒドロキシ脂肪酸は分子中のヒドロキシまたはヒドロキシアルキル基の位置が異なるのみである。それらは一般に混合物の形で存在する。天然の原料としての天然に存在する脂肪酸は本発明の目的に出発成分として好ましいが、これは対応するＣ鎖長を有する合成カルボン酸が適していないことを意味するものではない。

ポリ不飽和脂肪酸、例えばリノール酸、リノレン酸およびリシン酸も適している。ケイヒ酸を芳香族カルボン酸の具体例として述べ、酒石酸およびクエン酸をポリカルボン酸の例として述べる。

ポリヒドロキシ脂肪酸のヒドロキシアルコキシ成分はエポキシ化脂肪酸誘導体の開環に用いるポリオールから誘導される。好ましいポリヒドロキシ脂肪酸はそのヒドロキシアルコキシ基が24個までの炭素原子、特には12個までの炭素原子を有する好ましくは１級の二官能性のアルコールから誘導する。適したジオールはプロパンジオール、ブタンジオール、ペンタンジオールおよびヘキサンジオール、ドデカンジオール、好ましくはエタン－1,2－ジオール、ブタン－1,4－ジオール、ヘキサン－1,6－ジオール、重合度２～40を有するポリプロピレングリコール、ポリブタンジエンジオールおよび／またはポリエチレングリコールである。ポリプロピレングリコールおよび／またはポリテトラヒドロフランジオールおよびそれらの共重合生成物もジオール化合物として特に適している。これはこれらの化合物が約２～20の重合度を有している場合に特にあてはまる。しかしながら、トリオールまたはより多価のアルコールでさえも、例えばグリセロールおよびトリメチロールプロパンおよび1500までの分子量を有するそれらのエチレンオキサイドおよび／またはプロピレンオキサイド付加物も開環反応に用いてもよい。この場合には分子当たり２個を超えるヒドロキシル基を有するポリヒドロキシ脂肪酸が得られる。

ポリオールではなく、ヒドロキシカルボン酸、例えばクエン酸、リシノール酸、12－ヒドロキシステアリン酸、乳酸も開環反応用のヒドロキシ官能性化合物として用いてもよい。その場合には、エーテル基ではなくエステル基が生成する。アミン、ヒドロキシ官能性のアミンおよびアミノカルボン酸も開環に用いてよい。

しかしながら、ジヒドロキシ脂肪酸、特にジオールの、が好ましい。それらは室温で液体であり、他の反応物と容易に混合する。本発明においてはジヒドロキシ脂肪酸はエポキシ化不飽和脂肪酸の水による開環生成物、およびジオールによる対応する開環生成物並びに他のエポキシド分子とのその架橋生成物であると理解される。ジオールによる開環生成物も僅かにより正確にジヒドロキシアルコキシ脂肪酸と呼ぶ。ヒドロキシ基またはヒドロキシアルコキシ基はカルボキシ基から、少なくとも１、好ましくは少なくとも３、特には少なくとも6CH_2単位離れている。好ましいジヒドロキシ脂肪酸は9,10－ジヒドロキシパルミチン酸、9,10－ジヒドロキシステアリン酸および13,14－ジヒドロキシベヘン酸およびそれらの10,9－および14,13－異性体である。

本発明によりポリヒドロキシ脂肪酸を製造するために、エポキシ化カルボン酸エステル、例えばエポキシ化脂肪酸メチル、エチル、プロピルまたはグリセロールエステルを水および／またはそれからヒドロキシアルコキシ基が開環および所望によりエステル交換反応条件下に生成するポリオールと反応させる。好ましい態様では、反応すべきポリオールおよび／または水またはヒドロキシカルボン酸を、塩基性または酸性触媒、例えば強い鉱酸と共に最初に導入し、エポキシ化脂肪酸誘導体を、80～120℃の範囲の反応温度、塩基性触媒を用いる場合には200℃で連続的にまたは少しづつ加える。反応の進行は残存エポキシド含量を滴定することにより、または分光学的方法によりモニターする。エポキシ基が反応した場合、触媒は中和によりこわれる。このようにして生成したポリヒドロキシ脂肪酸エステルを蒸留により過剰の反応物から分離する。

第２の工程においてポリヒドロキシ脂肪酸エステルを通常ケン化し、ポリヒドロキシ脂肪酸を形成する。ケン化は水および触媒としての塩基の存在下に40～120℃の温度で好ましくは行う。適した塩基はアルカリ金属およ

び／またはアルカリ土類金属の水酸化物および３級アミンである。この反応工程の後に、ポリヒドロキシ脂肪酸を塩（ソープ）として蓄積し、強酸、例えば塩酸または硫酸の添加により回収する。反応生成物は水で一度または所望により数度洗浄することにより精製する。原理的には、水による加圧下での無触媒の、エステル特にトリグリセリドの開裂は可能である。

「アルコール」とは脂肪族および脂環式の、飽和、不飽和のおよび／または分岐の炭化水素のヒドロキシル誘導体であると理解される。一価および二価またはより多価のアルコールが適している。一価アルコールの外にこれらのアルコールはポリウレタン化学で公知の低分子量ヒドロキシ官能性の鎖延長剤または架橋剤を含む。低分子量範囲からの具体的な例は、ペンタノール、２－エチルヘキサノール、２－オクタノール、エチレングリコール、プロピレングリコール、トリメチレングリコール、テトラメチレングリコール、2,3－ブチレングリコール、ヘキサメチレンジオール、オクタメチレンジオール、ネオペンチルグリコール、1,4－ビス－ヒドロキシメチルシクロヘキサン、２－メチルプロパン－1,3－ジオール、ヘキサン－1,2,6－トリオール、グリセロール、トリメチロールプロパン、トリメチロールエタン、ペンタエリスリトール、ソルビトール、ホルミトール、メチルグリコシド、ブチレングリコール、還元されたダイマーおよびトリマー脂肪酸および高級なポリエチレン、ポリプロピレンおよびポリブチレングリコールである。

PUR化学で知られた他の有機ポリヒドロキシル化合物を高分子量化合物の製造に用いてもよい。このタイプの特に適した化合物は分子当たり２～10個のヒドロキシ基を有する60～10,000の範囲、好ましくは70～6,000の範囲の分子量を有する公知のポリヒドロキシポリエーテルである。このようなポリヒドロキシポリエーテルは、適当な出発分子、例えば水、プロピレングリコール、グリセロール、トリメチロールプロパン、ソルビトール、ケインシュガー、エタノールアミンまたはジエタノールアミン等のアミノアルコール、ヘキシルアミンまたは1,6－ジアミノヘキサン等の脂肪族アミンおよびそのような出発分子の混合物のアルコキシル化により公知の方法で得られる。適当なアルコキシル化剤は特にプロピレンオキサイドであり、場合によりエチレンオキサイドである。400～10,000の範囲の分子量を有する通常のポリエステルポリオールも、それらが２～６個のヒドロキシル基を有するなら発泡体の製造に用いてもよい。適当なポリエステルポリオールは、出発分子として例として既述したタイプの多価アルコールの過剰量と、コハク酸、アジピン酸、フタル酸、テトラヒドロフタル酸、ダイマーおよびトリマー脂肪酸またはそのような酸の混合物等の多塩基性の酸との公知の反応生成物である。ポリカーボネートポリオールも適している。

ａ）飽和および不飽和の脂肪酸とポリヒドロキシ化合物およびそのエトキシ化またはプロポキシ化誘導体との部分エステル、ｂ）飽和および不飽和の脂肪アルコール、ｃ）デンプン、糖およびセルロース並びにその誘導体、ｄ）エポキシ化トリグリセリドまたは脂肪酸エステルの、アルコール、カルボン酸、アミンおよび水による開環生成物および対応するアルコキシル化誘導体、並びにｅ）ヒマシ油またはヒマシ油誘導体を用いることも可能である。

アルコールの代わりに、多官能性の１級または２級アミン、アミノカルボン酸および低分子量タンパク質も鎖単位として用いてもよい。次のものを具体的な例として述べる:5,000までの分子量を有するポリオキシエチレン、ポリオキシプロピレンおよびポリオキシブチレンジアミン、またはグリシン、アラニン、バリン、ロイシン、システイン、シスチン、アスパラギン酸、グルタミン酸、チロシン、トリプトファン、β－アミノカプロン酸、11－アミノウンデカン酸、４－アミノ酪酸、モノーおよびジアミノナフトエ酸。

多官能性の芳香族および脂肪酸イソシアネートおよび／またはそれから製造したNCO末端のオリゴメリ化生成物をプラスチックの製造に用いる。「多官能性」とは1.5以上のイソシアネート成分の官能価を意味する。イソシアネート成分は、厳密に一官能性のイソシアネート、例えばフェニルイソシアネートを用いるイソシアネートの混合物であってもよい。

適当な多官能性イソシアネートは好ましくは平均して２ないし最大で５、好ましくは４個までのNCO基を有する。次のものを適当なイソシアネートの例として述べる：フェニルイソシアネート、1,5－ナフチレンジイソシアネート、4,4'－ジフェニルメタンジイソシアネート（MDI）、水素化MDI（H_{12}MDI）、キシレンジイソシアネート（XDI）、ｍ－およびｐ－テトラメチルキシレンジイソシアネート（TMXDI）、4,4'－ジフェニルジメチルメタンジイソシアネート、ジーおよびテトラアルキルジフェニルメタンジイソシアネート、4,4'－ジベンジルジイソシアネート、1,3－フェニレンジイソシアネート、1,4－フェニレンジイソシアネート、トリレンジイソシアネート（TDI）の異性体、場合により混合物、１－メチル－2,4－ジイソシアネートシクロヘキサン、1,6－ジイソシアネート－2,2,4－トリメチルヘキサン、1,6－ジイソシアネート－2,4,4－トリメチルヘキサン、１－イソシアネートメチル－３－イソシアネート－1,5,5－トリメチルシクロヘキサン（IPDI）、塩素化およびブロム化ジイソシアネート、リン含有ジイソシアネート、4,4'－ジイソシアネートフェニルパーフルオロエタン、テトラメトキシブタン－1,4－ジイソシアネート、ブタン－1,4－ジイソシアネート、ヘキサン－1,6－ジイソシアネート（HDI）、ジシクロヘキシルメタンジイソシアネート、シクロヘキサン－1,4－ジイソシアネート、エチレ

ンジイソシアネート、フタル酸ービスーイソシアネートエチルエステル;1ークロロメチルフェニルー2,4ージイソシアネート、1ーブロモメチルフェニルー2,6ージイソシアネート、3,3ービスークロロメチルエーテルー4,4'ージフェニルジイソシアネート等の反応性ハロゲン原子を有するポリイソシアネート。イオウ含有ポリイソシアネートは例えば2モルのヘキサメチレンジイソシアネートと1モルのチオジグリコールまたはジヒドロキシジヘキシルサルファイドとの反応に得られる。他の重要なジイソシアネートはトリメチルヘキサメチレンジイソシアネート、1,4ージイソシアネートブタン、1,12ージイソシアネートドデカンおよびダイマー脂肪酸ジイソシアネートである。自己架橋性のポリウレタンを形成できる部分的にマスクしたポリイソシアネート、例えば二量体のトリレンジイソシアネート、例えばフェノール、ターシャリーブタノール、フタルイミド、カプロラクタムと完全に、または部分的に反応したポリイソシアネートも興味がある。

一つの特別な態様においては、イソシアネート成分はダイマー脂肪酸イソシアネートを部分的に含む。ダイマー脂肪酸とは、オレイン酸、タル油脂肪酸またはリノール酸等の不飽和C_{18}モノカルボン酸の熱的または触媒的二量化により製造される、主にC_{36}ジカルボン酸の混合物であると理解される。ダイマー脂肪酸は当業者に良く知られており、商業的に入手し得る。ダイマー脂肪酸はダイマー脂肪酸イソシアネートへ反応できる。工業用ダイマー脂肪酸ジイソシアネートは、平均して、ダイマー脂肪酸分子当たり少なくとも2つの、そして3未満のイソシアネート基を含有する。好ましい態様においては、イソシアネート成分a)のうち30重量%以上、特にはイソシアネート成分a)のうち少なくとも大部分および好ましくは全部がMDI等の芳香族のイソシアネートよりなる。

芳香族イソシアネートが、上述したイソシアネートとポリオール、ポリアミンまたはアミノアルコールとのオリゴメリ化されたNCO末端の付加物と同様一般的に好ましい。しかしながら、予期しないことに脂肪族および脂環式イソシアネートも室温で速く、そして完全に反応できる。

多官能性イソシアネートをポリヒドロキシ脂肪酸と反応させる場合には、イソシアネート基(NCO)の活性水素を有する基(ACH)に対する当量比は2:1〜0.5:1、好ましくは1.5:1〜0.6:1であるべきである。活性水素を有する化合物との上述した反応の外に、過剰のイソシアネート基の三量化が必要なら、NCOの活性水素に対する比は5:1までである。

本発明による触媒は、正荷電を安定化させるそれらの能力によって、それらが非常に求核的であることにより特徴づけられる。この性質は脂肪族3級アミン、特に環状構造のものにおいて著しい程度に存在する。3級アミンの中で、イソシアネート反応性の基、特にヒドロキシル基および/またはアミノ基をさらに有するものも適している。次のものを具体的に述べる:ジメチルモノエタノールアミン、ジエチルモノエタノールアミン、メチルエチルモノエタノールアミン、トリエタノールアミン、トリメタノールアミン、トリプロパノールアミン、トリブタノールアミン、トリヘキサノールアミン、トリペンタノールアミン、トリシクロヘキサノールアミン、ジエタノールメチルアミン、ジエタノールエチルアミン、ジエタノールプロピルアミン、ジエタノールブチルアミン、ジエタノールペンチルアミン、ジエタノールヘキシルアミン、ジエタノールシクロヘキシルアミン、ジエタノールフェニルアミンおよびそのエトキシ化およびプロポキシ化生成物、ジアザビシクロオクタン(ダブコ(Dabco))、トリエチルアミン、ジメチルベンジルアミン(デスモラピッド(Desmorapid)DB、バイエル(Bayer)AG)、ビスージメチルアミノエチルエーテル(キャタリスト(Catalyst)AI、VCC)、テトラメチルグアニジン、ビスージメチルアミノメチルフェノール、2,2ージモルホリノジエチルエーテル、2ー(2ージメチルアミノエトキシ)ーエタノール、2ージメチルアミノエチルー3ージメチルアミノプロピルエーテル、ビスー(2ージメチルアミノエチル)ーエーテル、N,Nージメチルピペラジン、Nー(2ーヒドロキシエトキシエチル)ー2ーアザノルボルナン、テキサキャット(Texacat)DPー914(テキサコ・ケミカル)、N,N,N,Nーテトラメチルブタンー1,3ージアミン、N,N,N,Nーテトラメチルプロパンー1,3ージアミン、N,N,N,Nーテトラメチルヘキサンー1,6ージアミン。

しかしながら、特に環中に少なくとも1つの窒素原子を有し、正の誘電効果および/または正のメソメリー効果を有する他のヘテロ原子または官能基を有する場合には、ヘテロアロマティック(heteroaromatic)アミンを好ましくは用いる(エッチ・アール・クリステン(H.R. Christen)、グルンドラーゲン・デル・オーガニッシェ・ヘミー(Grundlagen der Org.Chemie、第4版、1977年、378頁以降)。例えばアルキル基は緩やかな正の誘導(+I)効果を有する。アミノ基は遊離電子対によって強い正のメソメリー(+M)効果を有する。したがって、好ましい触媒は+Iおよび/または+M効果を有する、特には更なるヘテロ原子を有する置換基を有するヘテロアロマティックアミンであり、それ故、正の荷電を特に効果的に安定化できる。そのような触媒の例は、ピロール、インドリジン、インドール、イソインドール、ベンゾトリアゾール、カルバゾール、ピラゾール、イミダゾール、オキサゾール、イソオキサゾール、イソチアゾール、トリアゾール、テトラゾール、チアゾール、ピリジン、キノリン、イソキノリン、アクリジン、フェナンスリジン、ピリダジン、ピリミジン、ピラジン、トリアジンの誘導体、および対応する構造元素を有する化合

物である。触媒はオリゴメリ化またはポリメリ化した形、例えばN－メチル化ポリエチレンイミン、として存在してもよい。

1－メチルイミダゾール、2－メチル－1－ビニルイミダゾール、1－アリルイミダゾール、1－フェニルイミダゾール、1,2,4,5－テトラメチルイミダゾール、1－（3－アミノプロピル）－イミダゾール、ピリミダゾール、4－ジメチルアミノピリジン、4－ピロリジノピリジン、4－モルホリノピリジン、4－メチルピリジンおよびN－ドデシル－2－メチルイミダゾールは特に適している。好ましい触媒はアミノ置換ピリジンおよび／またはN－置換イミダゾールである。

上述した出発物質および触媒は次の量比で用いる：イソシアネート1当量に対し、0.1～5、好ましくは0.1～2当量のカルボン酸およびアルコールの混合物、0.0001～0.5、好ましくは0.001～0.1当量のアミン、酸に対するアルコールの比は20:1～1:20である。イソシアネート反応性の基、特にOHおよびNH基をそれ自体で有する触媒を用いる場合、触媒は比較的高濃度で用いる。何故なら、触媒自体が分子量を高めるのに寄与するからである。この場合には、0.001～2.0当量のアミンを用いてもよい。

アルコールまたは多官能性のアミンが反応に含まれない場合、すなわち、イソシアネートがカルボン酸と反応する場合には、次の規則があてはまる：イソシアネートの1当量に対し、0.1～4、好ましくは0.8～1.4当量のカルボン酸、および0.001～0.5、好ましくは0.001～0.1当量の3級アミンを用いる。

化学量論的な組成および反応物の選択も架橋密度に影響する。従って、当業者は公知の方法で熱可塑性樹脂および熱硬化性樹脂の両方を製造できる。

多官能性のイソシアネートを主にヒドロキシカルボン酸と反応させる場合、アミンはヒドロキシカルボン酸とイソシアネートの和を基準にして好ましくは0.05～15重量%、より好ましくは0.5～10重量%の濃度で用いるべきである。

3級アミンの外に、他の触媒、特にカルボン酸のスズ（II）塩などの有機金属化合物、アルカリ金属水酸化物、アルコレートおよびフェノレート等の強塩基、例えばジ－n－オクチルスズメルカプタイド、ジブチルスズマレエート、ジアセテート、ジラウレート、ジクロライド、ビス－ドデシルメルカプタイド、スズ（II）アセテート、エチルヘキソエートおよびジエチルヘキソエートまたはフェニルエチルジチオカーバメート鉛を加えてもよい。あるカルボン酸、すなわちヒドロキシーおよびアミノカルボン酸を用いるなら有機金属触媒を単独で用いてよい。DABCO、TMR－2（エア・プロダクツ）等－エチルグリコールに溶解した4級アンモニウム塩－を三量化触媒として述べる。

脂肪族3級アミンの場合には、水は更なる発泡剤および鎖延長剤として最良である。しかしながら、他の公知の鎖延長剤も加えてもよく、それには次のものがある。

－エチレングリコールまたはエチレングリコール縮合物、ブタン－1,3－ジオール、ブタン－1,4－ジオール、ブテンジオール、プロパン－1,2－ジオール、プロパン－1,3－ジオール、ネオペンチルグリコール、ヘキサンジオール、ビス－ヒドロキシメチルシクロヘキサン、ジオキシエトキシハイドロキノン、テレフタル酸ビス－グリコールエステル、コハク酸ジ－2－ヒドロキシエチルアミド、コハク酸ジ－N－メチル－（2－ヒドロキシエチル）－アミド、1,4－ジ－（2－ヒドロキシメチルメルカプト）－2,3,5,6－テトラクロロベンゼン、2－メチレンプロパン－1,3－ジオール、2－メチルプロパン－1,3－ジオール等の通常の飽和および不飽和グリコール；

－エチレンジアミン、ヘキサメチレンジアミン、1,4－シクロヘキシレンジアミン、ピペラジン、N－メチルプロピレンジアミン、ジアミノジフェニルスルホン、ジアミノジフェニルエーテル、ジアミノジフェニルジメチルメタン、2,4－ジアミノ－6－フェニルトリアジン、イソホロンジアミン、ダイマー脂肪酸ジアミン、ジアミノジフェニルメタンまたはフェニレンジアミンの異性体等の脂肪族、脂環式および芳香族ジアミン；ジカルボン酸のカルボヒドラジドまたはヒドラジド；

－エタノールアミン、プロパノールアミン、ブタノールアミン、N－メチルエタノールアミン、N－メチルイソプロパノールアミン；ジエタノールアミン、トリエタノールアミンおよびジ－またはトリ－（アルカノールアミン）等のアミノアルコール；

－グリシン、1－および2－アラニン、6－アミノカプロン酸、4－アミノ酪酸、モノ－およびジアミノ安息香酸異性体、モノ－およびジナフトエ酸異性体等の脂肪族、脂環式、芳香族および複素環式モノ－およびジアミノカルボン酸。

さらに、フィラー、繊維、顔料、可塑剤、泡安定剤、気泡制御剤、難燃材、アンチアガー、ビターサブスタンスおよび殺菌剤等の典型的な添加剤を反応混合物に用いてもよい。

炭酸ガスの脱離が始まる反応温度は100℃未満、好ましくは50℃未満、より好ましくは35℃未満である。特には型でさえ予熱する必要がない。反応物をこの温度で混合するか、外部から熱を加えることにより混合物をこれらの温度にするだけで十分である。

反応は好ましくは室温、すなわち20℃±15で開始する。例えば密度を減少させ、さらに反応を促進するためには、30～70℃に出発の反応混合物を加熱するのが有利である。しかしながら、例えばイミダゾール誘導体若しくはジメチルアミノピリジン誘導体または高い濃度範囲の他の触媒を用いて、ある組成物は明らかに5℃未満の温度で発泡できる。

反応時間は、特に触媒およびその濃度の選択により、広範囲に変えることができ、かくして個々の応用に適合させることができる。加熱なしでは反応時間は、反応物の混合から開始して実質的に完全な硬化まで、24時間未満、好ましくは２時間未満、より好ましくは0.5時間未満である。室温（20±15℃）ではしかしながら15秒未満の反応時間でさえ十分である。

一般に反応物、すなわちイソシアネートおよびカルボン酸またはヒドロキシカルボン酸、アミノカルボン酸、および場合によりアルコールおよび多官能性アミンおよび３級アミンは前もって互いに反応させることなく同時に一緒にしてもよい。混合物を次に例えば開放型中またはベルト上でさらに加工して、スラブまたはサンドイッチエレメントを形成させてもよい。しかし反応混合物は、スプレー、注型または塗布により基材に塗布して、永久絶縁層を形成させてもよい。したがって、本発明による方法は基材をコーティングするために、特にラッカー吹付塗するために用いてもよい。発泡体を適当なタンクリアクター中で製造する場合、発泡体を脱ガスし、および／または攪拌して、公知の方法で成形品へさらに加工する、実質的に発泡していないプラスチックを製造することは可能である。

しかしながら、個々の成分を混合し、または互いに前もって反応させてもよい。例えばカルボン酸とアルコールとの混合物またはカルボン酸とイソシアネートとの混合物またはカルボン酸とアミンの混合物である。

本発明の組成物は反応射出成形（RIM）による加工に特に適している。この目的のために成分を素早く計量し、混合し、混合物を型（またはキャビティ）中に射出する。その中で組成物は型または反応混合物の温度によって数秒～数分以内に硬化する。一体発泡成形体がこの方法で製造できる。流延用コンパウンドも本発明の方法により製造できる。

しかしながら、発泡体を好ましくは製造する。これに関して気泡安定剤、例えばシロキサン／オキシアルキレン共重合体をベースにした気泡安定剤を用いるのが有用である。しかしながら、他のシリコンを含有しない安定剤、例えば、エア・プロダクツ社（Air Products）のLK－221（OH価40.5）、LK－332（OH価35）およびLK－443（OH価44）を用いること、または安定剤を全く用いないことも可能である。さらに発泡体が最大で800、好ましくは最大で250、より好ましくは最大で80g/lの密度を持ち得ることは驚くべきことである。

得られるプラスチックまたは発泡体は、40未満、特には10未満の小さい酸価により区別できる。

アミド基の外に、発泡体は、多官能性のイソシアネートがアミン基またはH_2Oと反応した場合に、尿素基を有する。アミド基の外に発泡体は、多官能性のイソシアネートがポリオールと、またはポリヒドロキシカルボン酸と反応した場合に、ウレタン基を有する。アミド基の外に、発泡体は、多官能性イソシアネートがカルボン酸およびアルコールと反応した場合に、エステル、尿素およびウレタン基を有する。

更なる長所は、硬質および半硬質のプラスチックおよび発泡体の外に軟質のプラスチックおよび発泡体も容易に製造できるという事実である。それらは射出成形物品、例えばカップ、受皿およびハウジングの製造に、または繊維およびフィルムの製造に特に適している。それらは、例えばフィルターを製造できる連続気泡発泡体の製造にも適している。

実際上、発泡速度が触媒濃度によりある程度まで影響され得ることは特に重要である。同じことは密度にもあてはまる。従って、本発明による発泡体は２成分の構造用発泡体およびアセンブリ発泡体の製造に特に適している。この場合にはポリヒドロキシカルボン酸の発泡体の改良された燃焼特性も有利である。

本発明による発泡体は、特にその密度が100kg/m^{3}未満、好ましくは25～50kg/m^{3}の範囲にある場合、２成分の構造用発泡体およびアセンブリ発泡体としての使用に適している。発泡体の低密度もそれらを絶縁および包装に使用する場合に、重要な要素である。この場合には密度は70kg/m^{3}未満以下であるべきである。

発泡体を、化学量論の変形により当業者に知られた原理の下で（高度の架橋）製造し、および好ましくは連続気泡および脆性構造が得られるような方法で気泡を連続させるための添加剤（例えばシリコン）を添加して製造するなら、この方法で得られる発泡体はフラワーアレンジメント発泡体としても用いてもよい。

本発明による方法は、断熱板、模型製造用の板、サンドイッチ要素、マットレスの製造に、またはモデリング発泡体として特に適している、少なくとも0.5mの高さ、幅および深さを有する大きい、硬質または弾性のスラグを作るのに難燃剤なしでさえ用いてもよい。

本発明による方法は、塗布した時に発泡する、特に良好な隙間をつなぐ効果によって区別される、接着剤および封止用コンパウンドの製造にも適している。

本発明を次の実施例によって説明する。

A:多官能性イソシアネート／多塩基性カルボン酸系の実施例

様々なポリカルボン酸とMDIとの室温での反応および得られる密度。断らない限り固体はエタノールに溶解する。

a)混合物:　１５g　ダイマー脂肪酸
(エムポル(Empol)１０１６、酸価１９２)
０.９２g　シリコーン界面活性剤
(テゴスタブ(Tegostab)Ｂ８４０４)
７.８８g　ＭＤＩ(デスモデュール(Desmodur)ＶＫＳ)

触媒	量 (g)	密度 (g/l)	クリーム時間 (秒)
１－メチルイミダゾール	0.12	53.5	59
４－ジメチルアミノピリジン (３３%溶液)	0.24	85.3	105
トリブチルアミン	0.12	281.2	>240
ジメチルベンジルアミン	0.12	242.6	>240
２,２'－ジモルホリノジエチルエーテル	0.12	289.2	>240
N,N'－ジメチルピペラジン	0.2	241.4	>240
２－(２－ジメチルアミノエトキシ)－エタノール	0.12	359.8	>240
モルホリン	0.12	507.8	>240

b) 混合物:　１５．９g　　トリマー脂肪酸

（ＶＴ２１３、酸価１８１）

0．９２g　　シリコーン界面活性剤

（テゴスタブＢ８４０４）

7．9g　　ＭＤＩ(デスモデュール·ＶＫＳ)

触媒

触媒	量 (g)	密度 (g／l)	クリーム時間 (秒)
１－メチルイミダゾール	0.12	70.9	90
４－ジメチルアミノピリジン（３３%溶液）	0.36	87.4	＞240
トリブチルアミン	0.12	217.1	＞240
ジメチルベンジルアミン	0.12	221.2	＞240
２，２'－ジモルホリノジエチルエーテル	0.12	236.4	＞240
２－（２－ジメチルアミノエトキシ）－エタノール	0.12	189.6	＞240
モルホリン	0.12	453.6	＞240
ピリジン	0.12	143.5	＞240

c) 混合物：　１５g　　アジピン酸／プロパン－１，２－ジオール ポリエステル（4：3、酸価１７８）

０．９２g　　シリコーン界面活性剤（テゴスタブＢ８４０４）

7．８８g　　ＭＤＩ（デスモデュールＶＫＳ）

触媒

触媒	量 (g)	密度 (g／1)	クリーム時間 (秒)
1－メチルイミダゾール	0.12	57.5	50
4－ジメチルアミノピリジン（３３％溶液）	0.12	69.1	70
4－ジメチルアミノピリジン（３３％溶液）	0.36	54.8	34
4－ピロリジノピリジン（５０％溶液）	0.12	71.6	70
2－（2－ジメチルアミノエトキシ）－エタノール	0.12	162.7	

d) 混合物：　１０．８g　　アジピン酸／ネオペンチルグリコール ポリエステル（4：3、酸価１５５）

０．７５g　　シリコーン界面活性剤（テゴスタブＢ８４０４）

７．９g　　ＭＤＩ（デスモデュールＶＫＳ）

触媒

触媒	量 (g)	密度 (g／1)	クリーム時間 (秒)
1－メチルイミダゾール	0.12	71.5	41
4－ジメチルアミノピリジン（３３％溶液）	0.36	52.9	20
モルホリン	0.12	258.5	＞200
ピリジン	0.12	141.9	120

B:多官能性ポリイソシアネート／カルボン酸／アルコール系の実施例

1.触媒として３級アミンを用いたヘキサメチレンジイソシアネートとダイマー脂肪酸VD52およびデスモフェン555Uとの反応

a)出発混合物

ーカルボン酸		5g ダイマー脂肪酸VD52
ーアルコール		10g デスモフェン(Desmophen)550U
ーイソシアネート		15g ヘキサメチレンジイソシアネート
ー触媒	実施例1	触媒なし
	実施例2	ジエタノールアミン1.0g
	実施例3	N−メチルイミダゾール1.0g
	実施例4	4−ピロリジノピリジン1.0g (不均一な反応混合物)

	実施例1	実施例2	実施例3	実施例4
b)温度				
出発温度[℃]	25	25	25	25
15分後の温度	26	34	39	45 (2分後)
c)混合物の外観				
1分後	透明、 液体	透明、 液体	透明、 液体、ガス発生	透明、 沈降
15分後	透明、 液体	曇り、 液体	泡立つ、 ゲル様	
20分後	透明、 液体	曇り、 液体	泡立つ、 ゲル様	
40分後	透明、 液体	曇り、 液体	泡立つ、 ゲル様	
24時間後	−	−	硬質、 発泡	硬質、 発泡
d)CO_2発生				
始まり	なし	なし	1分	1分
終了	−	−	20分	4分

2. 触媒の関数としてのPUR発泡体の密度

a)出発混合物

－アルコール	１０g（２４ミリモル)デスモフェン５５０U
－カルボン酸	１０g（３６ミリモル)オレイン酸(エデノール)(EDENOR)NRA)
－気泡安定剤	０.２g シリコーン界面活性剤
－イソシアネート	１５g デスモデュールＶＫＳ(ＭＤＩ)
－触媒	５.４ミリモル触媒

実施例５:	トリブチルアミン	１.０g
実施例６:	４－ジメチルアミノピリジン	０.７g
実施例７:	Ｎ－メチルイミダゾール	０.５g
実施例８:	ジエタノールアミン	９６g
実施例９:	４－ピロリジノピリジン	０.８g
実施例１０:	触媒なし	

成分は連続的に一緒にし、注意深く混合した(温度:室温２４℃)。

実施例	５	６	７	８	９	１０
b)密度[g／l]	１２６	４１	６０	６５０	４４	７８０
c)発泡体の酸価	２０	３	２１	－	５	－

3. 触媒の関数としての生成物組成

次の成分を連続的に一緒にし、注意深く混合した（温度：室温24℃）。反応混合物を約10分の反応時間の後にガスクロマトグラフィにより分析した。

a)出発混合物

－カルボン酸	カプリル酸	１.４g
－アルコール	２－オクタノール	１.３g
－イソシアネート	フェニルイソシアネート	２.４g
－触媒		

実施例１１: トリブチルアミン ３ミリモル

実施例１２: Ｎ－メチルイミダゾール ３ミリモル

実施例	１１	１２
CO_2 発生	弱	強
エステル[% 面積]	０	１６
アミド [% 面積]	２３	２８
ウレタン[% 面積]	３１	１８
残存酸 [% 面積]	１３	０

4. カルボン酸および触媒の関数としての密度および酸価

－カルボン酸	２０ミリモル	（ＣＯＯＨ）
－アルコール	６０ミリモル	（ＯＨ）8.４８g ＴＭＰ×５ ＰＯ（デスモフェン５５０Ｕ）
－安定剤	０.５２g	シリコーン界面活性剤
－イソシアネート	８３ミリモル	（ＮＣＯ）、１１.２８g ＭＤＩ（デスモデュールＶＫＳ）
－触媒	２ミリモル	

a)ギ酸（０.９２g）

触媒	量(g)	密度(g／l)	酸価
１－メチルイミダゾール	０.１６	３５.９	５.３
４－ジメチルアミノピリジン	０.２４	４０.４	６.１
４－ピロリジノピリジン	０.３０	４３.２	２.０
トリブチルアミン	０.３７	２５.４	７.９
ジメチルベンジルアミン	０.２７	２５.２	１.３

b)酢酸（１.２０g）

触媒	量(g)	密度(g／l)	酸価
１－メチルイミダゾール	０.１６	４０.８	１.７
４－ジメチルアミノピリジン	０.２４	４８.６	４.１
４－ピロリジノピリジン	０.３０	４８.９	６.８
トリブチルアミン	０.３７	２２２.８	３８.８
ジメチルベンジルアミン	０.２７	１６２.０	５２.２

c)カプリル酸（２.８８g）

触媒	量(g)	密度(g／l)	酸価	視覚的評価
１－メチルイミダゾール	０.１６	５２.４		硬質、混合気泡
４－ジメチルアミノピリジン	０.２４	４２.５	５.７	硬質、微細気泡
４－ピロリジノピリジン	０.３０	５０.８	６.５	硬質、微細気泡
トリエチレンジアミン（３３％、ジプロピレングリコール中）	０.６８	７３.９	１６.２	硬質、混合気泡
トリエチルアミン	０.２	１５９.９	４１.６	硬質、混合気泡

d)ナタネ油脂肪酸(エルカ酸少)5.64g

触媒	量(g)	密度(g/1)	視覚的評価
1-メチルイミダゾール	0.16	67.8	硬質、混合気泡
4-ジメチルアミノピリジン	0.24	67.9	軟質、微細気泡
4-ピロリジノピリジン	0.30	67.3	軟質、微細気泡
1-(3-アミノプロピル)-イミダゾール	0.25	66.8	硬質、混合気泡
ピリミダゾール	0.24	82.7	硬質、混合気泡
トリエチレンジアミン(33%、ジプロピレングリコール中)	0.68	103.9	硬質、混合気泡

e)

	量	OH価	酸価
トリエタノールアミン	2.98	1130	0
ナタネ油脂肪酸	5.56	0	200
混合物	8.54g	394	130
MDI(デスモデュールVKS)	11.75g	(5%過剰)	
1-メチルイミダゾール	0.13g		
テゴスタブB8484	0.41g		
全量:	20.83g		
理論密度:	46.81g/1		

微細気泡硬質発泡体、密度50g/1、非常に良好な機械的性質、非常に早い反応時間

f)

	量	OH価	酸価
アジピン酸/グリセロールの複合エステル	3.30	63	304
グリセロール×7EO	6.70g	400	100
混合物	10.00g	289	
MDI(デスモデュールVKS)	10.00g		
1-メチルイミダゾール	0.21g		
テゴスタブB8404	0.42g		
全量:	20.63g		
理論密度:	54.00g/1		

微細気泡硬質発泡体、密度56g/1

注:

テゴスタブ(Tegostab)B8404はポリシロキサン/ポリエーテル共重合体をベースにしたPUR気泡安定剤の商標(ゴールドシュミット(Goldshcmidt))である

C:多官能性イソシアネート/ポリヒドロキシカルボン酸系の実施例:

実施例についての一般的な観察:

出発物質を標準的なプラスチックのコニカル容器(容積220ml)に連続的に素早く秤量し、最後の添加後直ちに、手またはハイスピード撹拌器により約10秒間撹拌した。配合物中で示した量はグラムで表した重量部である。イソシアネート基(NCO)の活性水素を有する基(ACH)に対するモル比は必要なら表中に示す。すべての試験において周囲温度は22±2℃であった。反応は室温で

２時間後完全に完了した。試験は24時間後に行った。断らない限り実施例中で示した試験結果は22±２℃の試験温度に基づく。

A）使用したイソシアネートは、31.0重量％のNCO含量を有する室温で液体のジフェニルメタンシリーズの工業用ポリイソシアネート混合物であったデスモデュール（Desmodur）44V10、バイエル・アー・ゲー（BayerAG）の製品、実施例中では「MDI」と呼ぶ。）。

B）ポリオールは商業的に入手できるエポキシ化脂肪酸エステルと多価アルコールとの反応生成物である。ポリヒドロキシ脂肪酸の命名において

－最初の文字は出発エポキシドを示す：

Ｅ＝エポキシステアリン酸メチルエステル

－２番目の文字は反応物を示す

E:エチレングリコール

Z:クエン酸

－最初の３つのアラビア数字はmgKOH/gで表したOH価を表す。

－２番目の３つのアラビア数字はmgKOH/gで表した酸価を表す。

EZ－X00－158の製造

192g（0.8モル）のクエン酸および100gのエポキシステアリン酸メチルエステル（Ep.0=4.7%）を最初に導入し、撹拌しながら150℃に加熱後、さらに240gのエポキシステアリン（全体１モル）を20分かけて加えた。発熱反応において（170℃まで）混合物のEp.値は0.03%Ep.0に低下した。AV＝158、OHVは測定できなかった。

EE－158－173の製造

1,427g（4.2モル）のエポキシステアリン酸メチルエステル（Ep.0=4.7%）および130g（2.1モル）のエチレングリコールを、4.6gの濃硫酸存在下に撹拌しながら105℃に加熱した。反応は３時間後に終わった（Ep.0=0.19%）。触媒を4.6gのジエチルエタノールアミンで中和した。開環生成物を90℃で1,440gの15%水酸化ナトリウムで次にケン化した（反応時間２時間）。755gの35%硫酸を次に60℃で加え、有機層を水で２回洗浄し、真空で乾燥した。生成物は黄色の液体である（AV＝173、SV＝176、OHV＝158）。

EE－253－153の製造

53kgのエポキシステアリン酸メチルエステル（Ep.0=4.7%）および19.3kgのエチレングリコールを17gの濃硫酸存在下に撹拌しながら90℃に加熱した。最初に発熱した反応は1.5時間後終わった（Ep.0=0.03%）。触媒を88gの30%メタノール性ソジウムメチレート溶液で中和し、粗生成物を200℃まで真空で部分的に蒸留した（15.5kgの留出物）。黄色い透明な液体を得た（OHV＝235、SV＝159、AV＝0.1）。

53kgのエポキシステアリン酸メチルエステルのグリコールによる開環生成物を13.5kgの50%の水酸化ナトリウムおよび20kgの水で90℃でケン化した（反応時間約３時間）。次に23.6kgの35%硫酸を60℃で加え、有機層を水で２回洗浄し、真空で乾燥した。生成物（46.7kg）は黄色の液体である（AV＝153、SV＝162、OHV＝253）。

C）実施例で用いた気泡安定剤は600mPasの粘度（20℃）および52のOH価を有する加水分解安定性のポリシロキサン／ポリオキシアルキレン共重合体であった（「テゴスタブ（Tegostab）Ｂ－8404」、ゴールドシュミット（Goldschmidt）の製品）。

D）実施例において、使用した触媒は省略した形で述べた。触媒の省略名および知られている場合、化学名は次の表中に示す。構造の知られていない商業的に入手できる触媒の場合、または触媒混合物の場合には、化学名を商品名および製造者に置き換えた。

DMDEE　2,2'－ジモルホリノジエチルエーテル

NMI　Ｎ－メチルイミダゾール

DP－914　テキサキャット（Texacat）DP－914（ジプロピレングリコール中の脂肪族アミンの製品、CAS No. 25265－71－８）；テキサコ・ケミカル（Texaco Chemical）

実施例	1	2	3
ポリオールＥＥ－１５８－１７３	7.7	8.7	9.7
触媒　ＤＭＤＥＥ	0.1	0.1	0.1
シリコーン界面活性剤	0.2	0.2	0.2
ＭＤＩ	12.0	11.0	10.0
	20.0	20.0	20.0

実施例	1	2	3
発泡体の構造	微細気泡	微細気泡	微細気泡
密度　(kg／m³)	７１．８	７３．２	７８．０
室温での収縮	なし	なし	僅か

実施例	4	5	6
ポリオールＥＥ－１５８－１７３	１０．０	１０．０	１０．０
触媒　ＤＰ－９１４	０．２	０．５	１．０
シリコーン界面活性剤	０．２	０．２	０．２
ＭＤＩ	１０．０	１０．０	１０．０
	２０．４	２０．７	２１．２

実施例	4	5	6
クリーム時間　(秒)	５５	２７	１４
密度　(kg／m³)	８０．０	６０．０	５６．４
発泡体の構造	微細気泡	微細気泡	微細気泡
ＮＣＯ:ＡＣＨ比	１．２５:１	１．２５:１	１．２５:１

実施例	7	8	9	１０
ポリオール EE－253－153	９．０	１０．０	１１．０	１２．０
触媒　ＤＭＤＥＥ	０．１	０．１	０．１	０．１
シリコーン界面活性剤	０．２	０．２	０．２	０．２
ＭＤＩ	１１．０	１０．０	９．０	８．０
	２０．３	２０．３	２０．３	２０．３

実施例	7	8	9	10
密度　(kg／m³)	172	153	139	196
発泡体の構造	微細気泡	微細気泡	微細気泡	微細気泡
NCO:ACH比	1.71:1	1.40:1	1.15:1	0.93:1

実施例	11	12	13
ポリオールEE−253−153	10.0	10.0	10.0
シリコーン界面活性剤	0.2	0.2	0.2
触媒　NMI	0.2	0.5	1.0
MDI	10.0	10.0	10.0
	20.4	20.7	21.2

実施例	11	12	13
クリーム時間　(秒)	25	16	10
密度　(kg／m³)	52	54	49
発泡体の構造	中〜微細	中〜微細	中〜微細
機械的性質	半硬質	半硬質	半硬質

実施例	14	15	16	17
ポリオール EE−253−153	10.0	10.0	10.0	10.0
シリコーン界面活性剤	0.2	0.2	0.2	0.2
触媒　DP−914	1.0	1.0	1.0	1.0
水		0.10	0.2	0.4
MDI	10.0	10.0	10.0	10.0
	21.2	21.3	21.4	21.6

実施例	14	15	16	17
クリーム時間 (秒)	13	10	10	10
密度 (kg／m³)	61	47	36	33
発泡体の構造	微細気泡	微細気泡	微細気泡	微細気泡

実施例	18	19
ポリオール EZ－X00－158*	10.0	10.0
MDI	10.0	10.0
シリコーン界面活性剤	0.2	0.2
触媒 DP－914	1.0	0.5
	21.2	21.7

実施例	18	19
クリーム時間 (秒)	10	17
ライズ時間 (分)	2	3.5
粘着性のなくなる時間 (分)	2	10
密度 (kg／m³)	49.6	59.0
発泡体の構造	微細気泡	微細気泡

表について注記
－成分は重量部で示す。
－本発明による発泡体はアイボリーないしほとんど白色である。
－＊OH価は標準法によっては測定できなかった。

フロントページの続き

(51) Int. Cl.⁷	識別記号	FI	
C09J 177/00		C09J 177/00	
D01F 6/70		D01F 6/70	A
//(C08G 18/34		(C08G 18/34	
101:00)		101:00)	
C08L 77:00		C08L 77:00	

(31)優先権主張番号 P4242018.0
(32)優先日 平成4年12月12日(1992. 12. 12)
(33)優先権主張国 ドイツ（DE）

(72)発明者 クライン、ヨハン
ドイツ連邦共和国 デー－4000 デュッセルドルフ、ベートホーフェンシュトラアセ 1番

(72)発明者　グリュツマッヒャー、ローラント
ドイツ連邦共和国　デー―5603　ヴィルフラート、ハインリヒーハイネ・シュトラアセ　2番

(72)発明者　クラウク、ヴォルフガング
ドイツ連邦共和国　デー―4005　メールブッシュ　2、ノイエル・ヴェーク　30番

(56)参考文献　特開　平2－173027（ＪＰ，Ａ）
米国特許4016144（ＵＳ，Ａ）
米国特許3557027（ＵＳ，Ａ）
米国特許3620987（ＵＳ，Ａ）
英国特許908337（ＧＢ，Ｂ）
英国特許950876（ＧＢ，Ｂ）

(58)調査した分野(Int.Cl.^{7}，ＤＢ名)
C08G　18/34
C08J　5/18
C09D 177/00 - 177/10
C09J 177/00 - 177/10
D01F　6/70

4

PATENT SPECIFICATION

NO DRAWINGS

Inventors: ERWIN WINDEMUTH, GUNTHER BRAUN and PETER HOPPE

908,337

Date of Application and filing Complete Specification: May 25, 1960.

No. 18550/60.

Complete Specification Published: Oct. 17, 1962.

Index at acceptance:—Classes 2(5), R27K(2D:8D:9D), R32A, R32(B1:B2), R32C(1:5:6:8:10:12:14), R32D(1:2:3:4:5:6), R32(E1:E8:E9), R32G(1:2), R32H(1:2:3:5), R33C(1:5:6:8:10:12:14), R33(G:P); and 87(2), C1E2.

In

SPECIFICATION NO. 908,337

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are Erwin Windemuth of Friedrich-Bayer-Strasse 9, Leverkusen, Germany, Günther Braun of Kolner Strasse 361, Leverkusen, Germany and Peter Hoppe, Pfarrer-Kenemich-Platz 16, Troisdorf, Germany, all of German nationality.

THE PATENT OFFICE,
12th November, 1962

DS 67869/1(11)/R.109 200 10/62 PL

This invention relates to a process for the production of foam materials.

The processes which have become known in recent years for the production of foam materials with an isocyanate base can be divided into substantially two groups. In accordance with this classification, foam materials may be obtained by reacting the components of either of the following two groups of materials:

Group A: 1) Linear or branch compounds of relatively high molecular weight and containing OH groups,
2) A polyisocyanate, the quantity of which is usually equal to the amount required to react with the components mentioned under 1 and 3,
3) Water and
4) Activators.

Group B: 1) Linear or branched compounds of relatively high molecular weight and containing OH and/or COOH groups,
2) A polyisocyanate, the quantity of which is usually equal to the amount required to react with the components mentioned under 1 and, if desired 3.
3) Water, if desired,
4) Activators.

With the processes of group A, the carbon dioxide necessary for foaming purposes is obtained from the reaction of the polyisocyanate with water, and in the processes of group B the carbon dioxide is formed from the reaction of the polyisocyanate with COOH groups. In the limiting case when a linear component (1) is used, the result is an elastic foam material. In this case it is preferred to use a component (1) which has free OH groups, since in the processes involving carboxyl groups, difficulties arise with linear starting materials. Components (1) which are predominantly or exclusively free from COOH groups are consequently primarily used for the production of rigid or semi-rigid foam materials.

The present invention provides a process for the production of foam materials which comprises reacting at least one polyhydroxyl and/or polycarboxyl compound with a molecular weight greater than 300 and, if necessary or if desired (the latter case being when carboxyl groups are present), a compound which produces a blowing action under the reaction conditions, in the presence of a catalyst capable of polymerising isocyanates to form a perhydrotriazine ring, with more than twice the quantity of polyisocyanate which is required for reaction with the free hydroxyl and/or carboxyl groups and, if present and reactive, the compound which produces a blowing action under the reaction conditions.

A novel feature of this process, by comparison with the known processes hereinbefore referred to, consists in the use of the large excess of polyisocyanate, calculated on the reactive hydrogen atoms of the polyhydroxyl and/or polycarboxyl compounds (and

PATENT SPECIFICATION

NO DRAWINGS

Inventors: ERWIN WINDEMUTH, GUNTHER BRAUN and PETER HOPPE

908,337

Date of Application and filing Complete Specification: May 25, 1960.

No. 18550/60.

Complete Specification Published: Oct. 17, 1962.

Index at acceptance:—Classes 2(5), R27K(2D:8D:9D), R32A, R32(B1:B2), R32C(1:5:6:8:10:12:14), R32D(1:2:3:4:5:6), R32(E1:E8:E9), R32G(1:2), R32H(1:2:3:5), R33C(1:5:6:8:10:12:14), R33(G:P); and 87(2), C1E2.

International Classification:—C08g. C08j.

COMPLETE SPECIFICATION

A process for the production of Foam Materials

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT of Leverkusen-Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of foam materials.

The processes which have become known in recent years for the production of foam materials with an isocyanate base can be divided into substantially two groups. In accordance with this classification, foam materials may be obtained by reacting the components of either of the following two groups of materials:

Group A: 1) Linear or branch compounds of relatively high molecular weight and containing OH groups,

2) A polyisocyanate, the quantity of which is usually equal to the amount required to react with the components mentioned under 1 and 3,

3) Water and

4) Activators.

Group B: 1) Linear or branched compounds of relatively high molecular weight and containing OH and/or COOH groups,

2) A polyisocyanate, the quantity of which is usually equal to the amount required to react with the components mentioned under 1 and, if desired 3.

3) Water, if desired,

4) Activators.

With the processes of group A, the carbon dioxide necessary for foaming purposes is obtained from the reaction of the polyisocyanate with water, and in the processes of group B the carbon dioxide is formed from the reaction of the polyisocyanate with COOH groups and possibly with water. According to both groups of processes, soft and also rigid foam materials can be produced by a suitable choice of the structure of the components (1) containing OH and/or COOH groups. The hardness and brittleness of the foam materials is found to increase as the branching of the component (1) increases. In the limiting case when a linear component (1) is used, the result is an elastic foam material. In this case it is preferred to use a component (1) which has free OH groups, since in the processes involving carboxyl groups, difficulties arise with linear starting materials. Components (1) which are predominantly or exclusively free from COOH groups are consequently primarily used for the production of rigid or semi-rigid foam materials.

The present invention provides a process for the production of foam materials which comprises reacting at least one polyhydroxyl and/or polycarboxyl compound with a molecular weight greater than 300 and, if necessary or if desired (the latter case being when carboxyl groups are present), a compound which produces a blowing action under the reaction conditions, in the presence of a catalyst capable of polymerising isocyanates to form a perhydrotriazine ring, with more than twice the quantity of polyisocyanate which is required for reaction with the free hydroxyl and/or carboxyl groups and, if present and reactive, the compound which produces a blowing action under the reaction conditions.

A novel feature of this process, by comparison with the known processes hereinbefore referred to, consists in the use of the large excess of polyisocyanate, calculated on the reactive hydrogen atoms of the polyhydroxyl and/or polycarboxyl compounds (and

of the compound producing a blowing action if present). This compound producing a blowing action under the reaction conditions is referred to herein as a blowing agent. The difference as regards the hitherto usual processes becomes particularly clear from the fact that, by the new working procedure, rigid foam materials can also be produced from linear compounds containing carboxyl groups. This is possible because of the large excess of polyisocyanate together with special activators which trimerise the polyisocyanate to form perhydrotriazine rings. By this means, numerous cross-linking centres are formed, and depending on the amount of the polyisocyanate excess, the extent of the cross-linking of the final product can be varied.

In contrast hereto, with the known processes of groups A and B, the branchings which largely determine the properties of the final products are already present in the components (1). For example, if rigid foam materials were to be produced, the components (1) already had to be branched to a high degree and have a large content of reactive hydrogen atoms. This requirement involved a very undesirable high viscosity of the components (1), which frequently also led to difficulties regarding the necessary homogenisation of the reaction products when using mechanical mixers and very often necessitated working at elevated temperatures. Furthermore, with these highly viscous components, it became necessary with machines to introduce, for example, gear wheel pumps for conveying purposes. These pumps had to be designed as high-grade special high-pressure pumps to maintain the necessary working pressures. The large differences in viscosity of the reaction components also made it necessary to displace the admission of the components into the mixing chamber by 1/50 to 1/300 of a second relative to one another, in order to obtain loss-free discharge of the reaction mixture. This involved considerable expense for electronic control with automatically operating machines.

On the contrary, the process according to the invention, enables components (1) having a relatively low viscosity and a small content of reactive hydrogen atoms to be used as starting material, since the high degree of cross-linking essential for the production of rigid foam materials is formed by cyclising the polyisocyanate excess during the foaming. The previously hindering difficulties in mixing the reactants are therefore very substantially reduced or entirely avoided.

The smaller difference in viscosity of the components, which can be achieved, and the conveying of the components at normal temperature or at only slightly raised temperatures (for example at a maximum of 35°C) facilitates the mixing of the components. In addition, it is possible to provide a more reliable control of the foaming speed, for example by modification of the activator system.

An additional advantage of the working method of the present invention is provided by the formation of the branches during the foaming. Since the polyisocyanate excess (based on the reactive hydrogen atoms of the polyhydroxyl and/or polycarboxyl compounds) largely determines the properties of the resulting foam materials, it is possible with one and the same hydroxyl and/or carboxyl group containing compound to produce foam materials having different properties, (such as for example soft, semi-rigid or rigid foam materials), merely by varying the excess of the polyisocyanate. This is naturally an advantage, since in the case of the known processes hereinbefore described, it was necessary to use special components (1) in each case to achieve the above object.

Furthermore, the formation of the perhydrotriazine rings as an essential feature of the process of the present invention usually produces a very desirable thermostability of the foam materials, since it is known that perhydrotriazine rings are thermostable. As a result, especially when using polycarboxyl compounds, it is possible to obtain foam materials with decomposition points higher than 200°C. This is of great importance, especially with moulded components subject to danger of fire, foams of all types or for sandwich constructions of light material.

The linear or branched polyhydroxyl and/or polycarboxyl compounds which are considered for carrying out the process can have greatly differing structures. Linear polyalkylene glycol ethers of different molecular weights, obtained for example by polymerising alkylene oxides (such as ethylene oxide, propylene oxide, 1,2 - or 2,3 - butylene oxide, styrene oxide, epichlorhydrin or tetrahydrofuran), are suitable. Those which are preferred have a molecular weight between 300 and 10,000, corresponding to hydroxyl numbers of approximately 373 to 11. Copolymers produced by using different alkylene oxides are suitable, as are mixtures of the homologous polymeric polyalkylene glycol ethers.

Linear or branched addition products are also to be mentioned, such as those obtained by addition of the alkylene oxides to, for example, polyfunctional alcohols, aminoalcohols, amines or acids. As examples of polyfunctional components for the addition of the alkylene oxides, the following are mentioned: Simple glycols (such as ethylene glycol, propylene glycol, butylene glycols, hexamethylene glycol, 1,10 - decanediol, thiodiglycol, N - methyl diethanolamine or N,N[1] - dimethyl - N,N[1] - dihydroxyethyl ethylene diamine), glycols of higher molecular weight (such as the aforementioned linear polymerisation products of alkylene oxides of

different molecular weight), glycerine, trimethylol propane, butanetriol, hexanetriol, pentaerythritol, hexitols and pentitols (such as xylitol and sorbitol), as well as triethanolamine, tetrahydroxyethylated aniline, ethanolamine, diethanolamine, N - alkyl - ethanolamines, aniline, *o*- , *m*- and *p* - phenylene diamines, ethylene diamine, tetramethylene diamine, hexamethylene diamine and piperazine. Also to be mentioned in this connection are hydroxycarboxylic acids (such as tartaric acid, malic acid, α,α - dihydroxyadipic acid, ricinoleic acid, and hydroxystearic acid), dicarboxylic acids of the formula

$$HOOC—(CH_2)_n—COOH,$$

in which n is a whole number larger than 1, butane - 1,2,3,4 - tetracarboxylic acid, bifunctional carboxylic acids, and carboxylic acids of higher function obtained by polymerisation of unsaturated fatty acids, unsaturated dicarboxylic or polycarboxylic acids obtained by diene syntheses with for example maleic acid anhydride and dienes, or the saturated acids obtainable therefrom by hydrogenation. In this class of compounds is included for example the adduct which is obtainable from levopimaric acid and maleic acid anhydride, and from which the corresponding tricarboxylic acid can easily be obtained.

Other suitable polyhydroxyl and/or polycarboxyl compounds are polyaddition compounds of polyacetals and olefines, such as those described in United Kingdom Patent Specification No. 866,323, and also polythioethers, which can be obtained in known manner by condensation of thiodiglycol and its derivatives with themselves or with other polyhydric alcohols which are free from sulphur.

Linear or branched carboxyl group containing, compounds of the general formula

$$HOOC—R^{1}—(RX)_n—R^{11}—COOH,$$

in which n is a whole number larger than 1, X represents an oxygen or sulphur atom, and in which R, R^1 and R^{11} represent an alkylene radical, which can contain urethane and/or ester groupings, can also be readily used in accordance with the invention. The compounds can be obtained from the starting materials containing the aforesaid hydroxyl groups by reaction with, for example, dicarboxylic acids or dicarboxylic acid anhydrides. In the above formula, R can also comprise alkylene side chains, which in their turn can carry terminal COOH groups.

Another large group of suitable starting materials comprises linear or branched polyesters containing OH and/or COOH groups, which polyesters are obtainable by known condensation processes from polyfunctional alcohols, aminoalcohols, hydroxy carboxylic acids, aminocarboxylic acids or lactams and polycarboxylic acids. Such polyesters or polyester amides can advantageously be made from, for example, the following compounds: by adapting the quantitative ratios of the individual components: Diethylene glycol, triethylene glycol or glycols of the general formula

$$HO.(CH_2.CH_2.O)_n.CH_2.CH_2.OH$$

in which n is a whole number larger than 1, propylene glycol or polypropylene glycols of the general formula

$$HO-\left[\begin{matrix}CH-CH_2O\\ | \\ CH_3\end{matrix}\right]_n \begin{matrix}-CH-CH_2-OH\\ | \\ CH_3\end{matrix}$$

in which n represents a whole number, butylene glycol, glycerine, trimethylol propane, hexanetriol, pentaerythritol, castor oil, ricinoleic acid, hydroxy stearic acid, adipic acid, phthalic acid, tetrachlorophthalic acid, dimeric polycarboxylic acids or polycarboxylic acids of higher function obtained by polymerisation of unsaturated fatty acids. Polyesters or polyester amides obtained from the aforesaid or other structural elements can of course also be modified with monofunctional alcohols, amines, carboxylic acids, or saturated or unsaturated fatty acids, such as for example oleic acid.

Furthermore, other OH-containing compounds are the products of silanols or siloxanes with linear or branched polyesters or polyethers, and also polyacetals with terminal OH groups which are available by known processes and which can also contain tertiary nitrogen atoms. Reference is also to be made to polymers containing hydroxyl groups which are obtained from ethylene and carbon monoxide by polymerisation under pressure and subsequent hydrogenation, as well as those which are obtained from compounds with polymerisable double bonds by concurrent use of for example allyl alcohol, acrylic acid or acrylic acid derivatives, maleic acid anhydride or maleic acid semi-esters.

Finally, decomposition products of natural products are suitable for the production of foam materials in accordance with the invention. Natural rubber which is substantially decomposed by the incorporation of OH and COOH groups is an example of such a product. Bifunctional or higher functional polymerised fatty acids can also be used without further modifications.

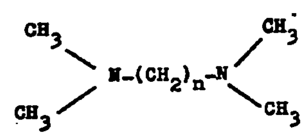
Since the foam materials are generally produced at room temperature, the components used should, for technical processing reasons, be liquid and have as low a viscosity at room

temperature as possible. A viscosity of 20,000 cP/25°C should not be exceeded. Naturally, components which have a higher viscosity or are solid at room temperature can also be processed. In these cases, the operation must be carried out at elevated temperatures at which the necessary homogenisation of the reactants is assured. However, elevated temperatures are only acceptable in those cases where the desired special properties of the resulting foam materials justify this.

It is also possible to use those compounds which contain, in addition to the OH and/or COOH groups, other reactive hydrogen atoms which can be detected by the Zerewitinoff method, such as for example amino groups with polyester amides.

Isocyanates suitable for the present invention are, for example, toluylene - 2,4 - diisocyanate; toluylene - 2,6 - diisocyanate; mixtures of the aforesaid diisocyanates, for example in the isomer ratio 80 : 20 or 65 : 35, and likewise the undistilled crude substances, and also 1 - alkyl - benzene - 2,4-diisocyanates; 2,6 - diethylbenzene - 1,4 - diisocyanate; 1 - methyl - 3,5 - diethylbenzene-2,4 - diisocyanate; *m* - phenylene diisocyanate; *p* - phenylene diisocyanate; diphenylmethane - $4,4^1$ - diisocyanate; diphenyldimethyl - methane - $4,4^1$ - diisocyanate; $2,2^1$-dimethyl - diphenylmethane - $4,4^1$ - diisocyanate; $3,3^1$ - dimethoxy - diphenyl - $4,4^1$-diisocyanate; $3,3^1$ - dimethyl - $4,4^1$ - diphenyl - diisocyanate; diphenyl - $4,4^1$ - diisocyanate; $3,3^1$ - dichloro - diphenyl - $4,4^1$-diisocyanate; naphthalene - 1,5 - diisocyanate; *m*- and *p* - xylylene - diisocyanates; 3 - (ω-isocyanatoethyl) - phenylisocyanate; hexamethylene diisocyanate; triphenylmethane-$4,4^1,4^{11}$ - triisocyanate; reaction products of polyhydroxy compounds with excess of a polyisocyanate, (for example a triisocyanate with an NCO content of 19.2% which may be obtained by reacting 1 mol of trimethylol propane and 3 mols of toluylene - 2,4 - diisocyanate); and isocyanate combinations which are partially polymerised giving some perhydrotriazine ring cyclisation. Moreover, monoisocyanates such as phenyl isocyanate, toluyl - isocyanates, or naphthyl - isocyanates, can be concurrently used with the polyisocyanates. These steps can very often produce valuable technical advantages and desirable modifications of the final products. It is preferred to use those aromatic diisocyanates of which the aromatic rings are unsubstituted in at least one neighbouring position or even in both neighbouring positions to the NCO group.

Catalysts were generally introduced into the prior art processes for the production of foam materials according to groups A and B and these catalysts could be of various organic or inorganic natures. With the process of the present invention, the introduction of catalysts is necessary in every case, and in some cases, these catalysts can also be incorporated into the polyhydroxyl and/or polycarboxyl compounds. The catalysts or catalyst combinations all have in common the capacity of polymerising isocyanates to form a perhydrotriazine ring. Combinations of tertiary amines with carbamic acid esters monosubstituted on the nitrogen atom (see United Kingdom Patent Specification No. 842,420 are effective. These combinations of tertiary amines are always present in the process of the invention when tertiary amines are used to form foam materials from starting materials containing hydroxyl groups. Furthermore, combinations of tertiary amines with methyl alcohol or methyl carbamate are suitable activators, since in accordance with United Kingdom Patent Specification No. 842,420, these constitute high-grade trimerisation catalysts for isocyanates. Aliphatic, cycloaliphatic or araliphatic tertiary amines are especially suitable, for example those of the general formula:



in which n represents a whole number greater than 1.

Further suitable amines are permethylated diethylene triamine or triethylene tetramine and amines of the general formula

$$R{-}N{<}\begin{matrix}CH_3\\CH_3\end{matrix},$$

in which R represents a linear or branched, saturated or unsaturated, aliphatic, hydroaromatic or araliphatic radical, which radicals can also contain hetero atoms such as oxygen, sulphur or nitrogen. Examples of this last-mentioned group are dimethyl butylamine, dimethylstearylamine, dimethyl - (3 - ethoxy)-propylamine, hexahydrodimethylaniline and dimethylbenzylamine; also suitable are methylmorpholine, 1,4 - diazabicyclo - (2,2,2,)-octane, N,N - dimethyl - piperazine, methyldimethylaminoethyl - piperazine.

Examples of tertiary amines incorporated into the polyhydroxyl and/or polycarboxyl compounds are addition products of alkylene oxides with monofunctional or polyfunctional amines, aminoalcohols or polyesters which have been produced using N - methyldiethanolamine. By using such starting materials, the additional use of other monomeric tertiary amines for the foaming often becomes superfluous.

Another group of high quality catalysts for the process of the invention are compounds,

which are in the position to form hydroxyl ions or substituted hydroxyl ions, and which can be represented by the general formula

$$R—O^{\ominus}Me^{\oplus}$$

in which R represents a hydrogen atom or an alkyl, aryl, aralkyl or cycloalkyl group, which groups may be linear or branched and which can also contain hetero atoms such as oxygen, sulphur or nitrogen, and may be substituted once or several times in the molecule. Furthermore, R can represent the grouping

$$R^1—CO—,\ R^1—CS—,\ R^1—CO—O—,$$
$$R^1—O—,\ R^1—CO—NH—,$$

in which R^1 is a hydrogen atom or an alkyl, aryl, aralkyl or cycloalkyl group. $Me^{\oplus}$ represents an alkali metal ion or a quaternary ammonium ion. The grouping $—O^{\ominus}Me^{\oplus}$ can also exist several times in one molecule. Also suitable, even if less effective, are activators of the general formula

$$2(R—O^{\ominus})Me^{\oplus\oplus},$$

in which $Me^{\oplus\ominus}$ represents a divalent metal ion.

Examples of such catalysts are alkali metal alcoholates (such as sodium polypropylene glycolates from linear or branched polypropylene glycol ethers), alkali metal phenolates (such as 2 - nitro - 4 - chlorophenyl sodium), alkali metal peroxides, alkali metal salts of monofunctional or polyfunctional carboxylic or sulphonic acids (such as potassium benzoate, potassium acetate, potassium oleate, potassium salts of polymerised linoleic fatty acid, sodium perbenzoate or the potassium salts of benzhydroxamic acid), zinc stearate, the sodium salt of a sulphonated castor oil or basically reacting alkali metal salts of inorganic acids (such as for example tertiary potassium phosphate or sodium borate).

Catalyst combinations which can be used with advantage are those which can be homogeneously mixed with or dissolved in the other reactants. Examples of these are alkali metal oleates in oleic acid, or alkali metal salts of polymerised unsaturated fatty acids. In addition to the often good solubility in the other reactants, such combinations have the additional advantage of being incorporated into the foam material to form carboxylic acid amide groups with the simultaneous evolution of carbon dioxide. This is best made clear by the fact that without any difficulties, as can be seen from the examples hereinafter described, a foam material can be obtained from a polyisocyanate and a polymerised unsaturated fatty acid containing alkali metal salts, without the addition of further polyhydroxyl and/or polycarboxyl compounds. The same also applies as regards certain alkali metal alcoholates, for example a sodium alcoholate of a linear polypropylene glycol ether having a molecular weight of 1200, dissolved in the same polypropylene glycol ether. With this activator combination also, a foam material can be produced in accordance with the process of the present invention without the addition of further polyhydroxyl and/or polycarboxyl compounds. In this case, however, the blowing gas necessary to produce a foam material must be formed by the concurrent use of a blowing agent, more especially water.

A second group of catalysts are alkali metal salts of monofunctional or polyfunctional carboxylic acid amides, (such as for example potassium phthalimide, sodium succinimide), and also alkali metal amine derivatives of the general formula

$$\begin{matrix} R^1 \\ & >N—Me, \\ R \end{matrix}$$

in which Me is an alkali metal, R and R^1 can be the same or different and represent alkyl, cycloalkyl, aralkyl or aryl groups, which can be linear or branched, saturated or unsaturated. Examples of these derivatives are sodium diphenylamide, sodium methyl aniline and lithium diethylamine.

Compounds which contain an alkali metal directly bonded to carbon, such as for example sodium phenyl, lithium butyl and sodium cyclopentadiene, are also suitable as catalysts in accordance with the invention, since in contact with the polyhydroxyl and/or polycarboxyl compounds or possibly with water, they are decomposed into effective activators for the present invention.

The activators can be used alone or in combination with one another, whereby additional effects are frequently produced. Furthermore, the concurrent use of activators which do not act preferentially to form a perhydrotriazine ring by polymerisation, can provide additional effects, such as the introduction of metal compounds, (for example iron acetyl acetonate and dialkyl tin dialcoholates which are soluble in the organic medium).

The catalysts indicated as being suitable for the process of the invention are those which are known as polymerisation catalysts for isocyanates. By polymerisation catalysts, there are understood in this connection compounds which are able to cyclise isocyanates forming trisubstituted perhydrotriazine rings. Even if the excess of isocyanate introduced is, for the major part, required by this cyclising reaction, (as shown by spectral analysis), other cross-linking reactions, (for example by way of urea, carboxylic acid amide or urethane groups), certainly also take place in addition to these cyclising reactions. This is allowed for by the formulation "for

cyclising and side reactions " in the following examples, when calculating the isocyanate balance for the isocyanate excess exceeding the index 100 (see below).

To produce the foam materials, a homogeneous mixture of the polyhydroxyl and/or polycarboxyl compounds, water and activators can be initially prepared by a proved working method, and the polyisocyanate added to this mixture. The amount of polyisocyanate must be very much greater than that necessary to react with the reactive hydrogen atoms which are present. In order to define this excess of polyisocyanate, the term " index " is introduced. If the quantity of isocyanate introduced is equivalent for the reaction of all reactive hydrogen atoms of the other reaction components, this quantity is allotted an index of 100. Consequently, with an index of 200, a quantity of isocyanate equal to twice the equivalent is used and with an index of 600, six times this quantity is used. The process of the invention includes only those combinations which work with an index greater than 200. It is quite usual to work with indexes of 500 to 1,000.

After adding the polyisocyanate, the reaction mixture starts to foam and solidifies into a foam material with a more or less strong heat of reaction. The speed of the foaming and the speed of the hardening or curing is naturally dependent on the nature of the starting materials and especially strongly dependent on the nature and quantity of the activator introduced. The setting process can easily be accelerated strongly in such a way that a solidification into foam material takes only a few seconds. The examples which follow give further details in this respect.

According to another form of the process, an initial adduct containing isocyanate groups and prepared from polyisocyanates and the polyhydroxyl and/or polycarboxyl compounds is produced with indices greater than 200, this adduct providing the foam material after admixing a blowing agent and a polymerisation catalyst.

The bulk density or weight per unit volume of the foam materials is substantially determined by the content of COOH groups and/or water in the foamable mixture. In addition, it is however also influenced by the nature and quantity of the catalyst and by the quantity of polyisocyanate introduced. It is found that as the heat of reaction increases during the foaming process, the bulk density of the foam materials tends to decrease.

As regards the economic production of very light foam materials which are improved in their behaviour as insulating materials, it can be advantageous to use solvents which are inert with respect to isocyanates as blowing agents. Mentioned as examples are acetone, ethyl acetate and tertiary butanol, as well as more especially halogenated saturated and/or unsaturated hydrocarbons with a boiling point lower than 200°C. for example trichlorofluoromethane, - 1,1 - dichlorethylene, *n* - propyl chloride, 1,2 - dichlorethylene, trichlorethylene, 1,2 - dichloropropane, tetrachloromethane, *n* - butyl chloride and 1,2-dichlorethane.

The use of blowing agents (other than water) which react with isocyanates to split off gas, such as for example aldoximes or those which decompose at relatively high temperature while splitting off gases, is likewise very often advantageous for the production of foam materials with low bulk densities. For example, acetaldoxime, butyraldoxime, isobutyraldoxime, sodium bicarbonate, ammonium carbonate, ammonium nitrite, hydrogen peroxide, dimethylol - *p* - cresol and substances splitting off formaldehyde such as paraformaldehyde have proved suitable. In similar manner, the blowing agents used in the rubber-processing industry for the production of foam rubber can also be used in the process of the present invention. Examples of these are: diazoaminobenzene, azodiisobutyric acid nitrile, azohexahydrobenzonitrile, azodicarboxylic acid diethyl ester and dinitrosopentamethylene tetramine. All these blowing agents can also be used together with water.

The concurrent use thereof is of especial interest in connection with the production of sandwich constructions of light-weight materials. In this case a subsequently occurring and thus graduated additional blowing action or an additional final blowing is desired after the hollow element has been filled with the still liquid reaction mixture for the foam material. This is to produce a careful inward pressing of the surface layer hollow construction into the supporting form, which is stable with respect to the foaming pressure set up. The said hollow construction advantageously is very thin and still capable of shaping or moulding to form a light structural element.

Additional means for lowering the bulk density of the foam materials is offered by the admixing of gases such as air, carbon dioxide or nitrogen during the foaming.

Colouring agents, such as organic or inorganic pigments, can be concurrently used in the same way as fillers, for example carbon black, silica gel, barium-sulphate, metal powder or cellulose. In addition, the foamable reaction mixtures can have added thereto foam stabilisers with a basis of organic silicon compounds, anion-active, cation-active or non-ionic emulsifiers as well as fire-proofing agents, such as trichlorethyl phosphate or generally haloalkyl phosphates, ammonium phosphates and phenol formaldehyde-dicyandiamide mixed condensates.

Occasionally, special effects are provided by adding plasticisers, if desired highly chlorinated paraffin hydrocarbons or phthalic acid esters.

In connection with moulded elements or core layers of composite constructions and made of foam materials, contrast agents may be added so that it is possible to detect, by means of illumination, any blow-holes which endanger the stability of the foam elements.

Excellent bonding capacity of the moulded elements of foam material is obtainable according to the invention with surface layers of all types using starting materials containing preferably carboxyl groups. Hence, with composite or sandwich elements made of light-weight material, which are not subject to too heavy stresses, it is possible to dispense with the pretreatment of the surface layers.

The process according to the present invention makes possible the production of foamable reaction mixtures which, also after a very rapid passage (up to 1/1000 of a second) through the known mixing chamber systems used in the art, suddenly yield a creamy consistency. Thus, large and complicated cavities in composite constructions or moulded elements of all types can easily be filled with foam in a homogeneous manner without leaving any streaks.

Reaction mixtures which swell with a creamy consistency are especially desirable for filling hollow elements with foam when the hollow elements comprise appropriate marginal zone reinforcements. The desired uniform impregnation of even relatively large constructional elements, both when the foam-filling operation takes place horizontally and vertically, is substantially facilitated when using reaction mixtures which blow with a creamy consistency.

The process can be carried out intermittently or in continuously operating apparatus. In the latter case, use is made of mechanical arrangements such as those described for example in French Patent Specification No. 1,074,713 and in United States Patent Specification No. 2,764,565.

According to one particular embodiment of the process, foam materials with an increased stability towards heat can be obtained by using polyethers or polyesters containing polymerisable double bonds. These may be foamed in the presence of other polymerisable components such as for example diallyl maleate, triallyl cyanurate, styrene or acrylic acid esters, and in the presence of polymerisation accelerators such as azodiisobutyric acid nitrile and ditertiary butyl peroxide.

Foam materials with an isocyanate base and having a selected dimensional stability at temperatures of from 50 to 200°C., a course or a fine pore structure and with a bulk density of 5—700 kg/m^3 can be continuously or intermittently foamed freely as block material or foamed as moulded elements which can be cut into sheets of all types by means of suitable cutting machines (for example band cutters, band saws or heated wire). The moulded elements can be subjected to a hot deformation and/or surface improvement of any suitable type (such as lacquering, fibre-coating, embossing or covering). It is also possible with block foaming, for the reaction mixture to be applied to, or between, sheets or slabs of synthetic or natural light-weight material such as balsa wood, or wood fibre board, whereby sheet or slab materials with an unsymmetrical or symmetrical structure can then be produced.

Sheets or slabs consisting solely of the foam materials are used for insulations of all types (for example heat, cold and sound insulations) in building constructions and in the construction of containers, vehicles, aircraft and ships. They may also be used as core layers of composite or sandwich constructions having a light core (which constructions are united by being stuck with surface layers of all types in a symmetrical or unsymmetrical formation), and can be used in building constructions and in the construction of vehicles, ships, boats, containers, refrigerators and furniture as flat or curved elements, for example as roofing slabs, wall slabs, doors, floors, coachwork components for rail and road vehicles, aircraft constructions, boats' hulls, ships' fittings, stationary and portable refrigerating containers of all types, tables, beds, cupboards and chairs. The core layers of the sandwich constructions can be locally reinforced on assembly to take up separate forces by filler bodies of relatively high strength.

The foam materials can be used for the production of moulded elements of all types and sizes, it being possible for these to be produced by casting in simple or multiple moulds, for example by centrifugal casting. If such moulded elements are subjected to local loads according to the purpose of use (for example anchoring forces, separate forces or fittings), the moulds are equipped prior to the foaming process with filler blocks, dowels or other attachments which withstand a high load, these being well enclosed during the foaming process, and are also well anchored as a result of the good bonding capacity which can be produced with the foamable reaction mixture. When using mixers with which quantities can be measured, the reaction mixture will preferably be introduced through small filling openings into the closed mould.

The supporting or bearing capacity of the moulded elements can be considerably increased by surface or internal reinforcement and thus can be adapted to the particular use. It is necessary in all cases that the reinforcing material can be satisfactorily surrounded by foam. Suitable for surface reinforcements, are felted fleeces of for example glass fibres, plastic fibres, natural fibres or metal fibres or combinations thereof, which in certain cases are so additionally bonded by stitching, that they cannot be forced apart by the penetrating

reaction mixture which forms the foam material. The moulds provided with release agents are suitably provided with for example an initial spray of adhesive with which the surface reinforcement is fixed to the mould wall, so that it is secured against floating off during the foaming process. Here also, locally arranged attachments consisting of materials having a higher strength factor can be used at certain places.

For a complete internal reinforcement of the core of the moulded element, or for a reinforcement thereof in certain zones, which internal reinforcement can also be used in conjunction with a surface reinforcement, it is preferred to use systems of materials of all types which can be thoroughly impermeated with foam. These systems can be constructed as, for example an exact frame work or irregularly tangled fibre mats.

Moulded elements thus partially or completely reinforced internally have an improved bearing capacity and rigidity due to the improved shearing strength of the foam material.

It is also possible to obtain moulded elements with or without surface or internal reinforcements by completely filling the moulds with filler bodies of all types and sizes, and by forcing foam into the free volume still existing between the irregularly disposed filler bodies. In this case it is preferred to introduce the reaction mixture, from which the foam material is formed, into the mould for filler bodies while the mould is still open in order to permit a good initial distribution of the reaction mixture, especially with components having a large surface. This also ensures a homogeneous foaming in the mould, which is closed after the foam has been introduced.

Moulded elements consisting of foam materials having an isocyanate base and manufactured by the above procedure are for example suitable for the following articles:

Packings of all types (moulded parts or formation of foam around the articles to be packed),
Domestic articles of all types,
Decorative articles for fabrics of all types,
Plastics (objects d'art, display window dolls or figures, decorative articles, body-correcting devices),
Toys of all types,
Hats and hat shapers,
Shoe heels, shoe soles, shoe lasts, complete shoes, and also plates, containers, shells, corrugated and hollow profiles of all types for all purposes in the construction of vehicles, ships and aircraft, the insulating industry, electrotechnical industry, mining, bridge constructions, road constructions, constructions below and above ground, hydraulic constructions, fishing and sporting equipment, machine and tool constructions, mould and weapon constructions, medicine, protheses and furniture constructions and life-saving equipment.

Because of the high degree of insensitivity of the foaming reaction mixture, the good bonding strength thereof to materials, the wide range of variation in the initial product for the purpose of obtaining the required bulk densities, stability under heat, freedom from shrinkage, water resistance, resistance to tropical conditions and the good static and dynamic properties, the foam materials are excellently suitable for filling hollow moulds or cavities. It is possible to fill moulds or cavities without applying pressure (free foaming), under a low foaming pressure (0.5 to 1.0 atm. gauge), and with a relatively high foaming pressure (1.0 to 10.0 atm. gauge), depending on expediency or the particular object in view.

For filling cavities with foam without applying pressure, for which it is very often not possible to use any separate supporting means, such as for example for insulations above and below ground, insulations in ship construction, insulations for refrigerating cars or for refrigerating vessels of large dimensions, the filling of pontoons, boats and floats of all types with foam, and for other purposes, it is preferred to use foam mixtures which in addition have low reaction temperatures of about 50°C. in the marginal zones (contact zones) and good bonding capacity with the surface materials actually surrounding the cavity (metal, plastic, wood or building materials of all types). Because of a sufficiently high index they do not show any primary shrinkage, so that no detachment from the hollow body or surface material of the cavity can occur with the cooling of the foam filling. Relatively low reaction temperatures of the blowing mixture are desirable in order for example to avoid deformation when unsupported hollow elements of deep-drawn plastic hollow bodies (for example refrigerator housings) are filled with foam, or to avoid the thermal stresses being too high with metallic surface layers (for example laminated insulations), which stresses could lead to changes in contour of the hollow constructions. Large cavities are filled with foam without using pressure by superimposing layers of foam which are separately supplied in measured quantities, whereby the lower viscosity of the applied reaction mixture makes possible a lamination which is free from bubbles and blow holes, and a lower reaction temperature permits a rapid sequence of the laminating processes. The hollow constructions to be filled with foam by a pressure-free process can generally not be subjected to any high stresses, since the bonding of the foam does not permit any strong support of the surface layer.

The filling process using foam pressures up to 0.5 to 1.0 atm. gauge is used for filling hollow bodies or cavities with foam by a single filling operation, the hollow body to be filled being supported by suitable devices or tensioning means for maintaining the contour. Small composite or sandwich elements are placed in multiple supporting devices and filled with foam by introducing measured quantities of the reaction mixture into a collecting chamber. The blowing mixture passes through this chamber filling ducts into the preferably centrally arranged hollow element, for which purpose it is also possible for example to use a centrifugal casting process.

For larger hollow bodies or elements, a foaming pressure of about 1.0 atm. gauge is always necessary in order to be able to control the usually necessary large rising or foaming paths. The filling process very frequently also serves additionally for inward pressing in order to obtain contours of the correct dimensions. The foaming pressure can be obtained by, for example, forcing a free foam specification of 50 kg./m^3 by over-supply to a final foam bulk density of 70—80 kg/m^3. The very liquid consistency of the blowing foam mixture supplied in excess quantity permits an accelerated filling of the cavity and, by pressure equalisation, a homogeneous bulk density distribution before the final cross-linking takes place.

For specific foams advantageously with components containing carboxyl groups, it is for example also possible for the desired foam pressure to be obtained with a very small excessive quantity by comparison with the free specification or recipe, this being achieved by retarding the COOH/NCO reaction. The low-pressure foaming process is also suitable for the continuous production of composite or sandwich elements of all types.

The filling of the hollow bodies or cavities with foaming pressures higher than 1.0 atm. gauge is necessary when plates, slabs or shelves, which have a large area and perhaps also a strong curvature are to be manufactured, or when it is desired to have light-weight composite constructions, which can be highly stressed so as to produce a high degree of safety against swelling such as is necessary for "light core sandwich constructions." For such light-weight constructions, marginal zone reinforcements of the foam supporting core, for example consisting of fibre fleeces of all types, can be initially mounted by sticking on the thin-walled surface layers. These are preferably used to increase the bonding between the core and the surface layer and for improving the E-modulus of the foam material. The reinforcements are thoroughly impregnated during the foaming process at increased foaming pressure and enable the production of a foam core which has a density in the marginal zone greater by several times than the interior of the foam core. Once again the increased foaming pressure can be obtained by oversupply or by graduating the course of the reaction.

The following examples are given as filling methods for prefabricated constructional elements or for foaming *in situ* (filling existing moulds, cavities or light-weight sandwich constructions having a light-weight core with foam) in which low or high foaming pressures are used, and according to particular requirements, and a low, mean or high supporting capacity of the filled construction can be produced:

Insulation field: for example refrigerator construction, refrigerator containers, large refrigerating plants, heat-resisting containers of all types, insulated moulded elements the insulation of walls, pipelines, troughs, containers or apparatus of various types by foaming *in situ* (the elements to be acoustically or thermally insulated being equipped prior to foaming with a permanent cover of for example metal or plastic, or with a movable shuttering) for constructions above and below ground, the construction of ships, apparatus, vehicles and aircraft and floats.

House construction and fittings: for example roofing slabs, roof shell construction, wall slabs, parapet slabs, doors, ceilings, windows and window frames, staircases, composite profiles for roof trusses, ceiling supports, skeleton structures and rollers blinds, and also baths, washbasins and pedestals.

Vehicle construction: large-surface bodywork components for road and rail vehicles (flat and curved sheets) with surface layers floor constructions, partitions, seat constructions, luggage compartments, windows, doors, instrument plates and cooling and heating assemblies and for safety devices.

Sea-travel: ships' fittings, (walls, doors, loading hatches, furnishing equipment), ships' insulations, boats' hulls, floats (for example buoys, rafts, life-saving equipment) and acoustic and thermal installations.

Aircraft construction: fuselage, wings, control equipment and fittings such as for example also light-weight crockery.

In addition, moulded elements, shelves, profiles in a light-weight core composite construction for electro-technical purposes, container construction domestic equipment and the toy industry all can use the foams of the present invention.

The following Examples further illustrate the present invention:

Example 1

Production of the initial material:

4000 Parts by weight of a linear polypropylene glycol ether with a hydroxyl number of 56 are heated with 584 parts by weight of adipic acid to a temperature of 200 to 205°C., (during the last eight hours in a vacuum of 12 mm. Hg.) 72 Parts by weight

of water are thereby split off with a steady decrease in the acid number from initially 97.7 to 47.5 at the end of the reaction period. After cooling, free adipic acid is precipitated in the viscous reaction product, and this is separated out. The somewhat yellowish-coloured oil filtrate has an acid number of 30.7, a hydroxyl number of 5.5 and a viscosity of 273 cP/75°C. and 2860 cP/25°C.

A foam material is obtained from this polypropylene glycol ether dicarboxylic acid if 100 parts by weight thereof are thoroughly mixed with 30 parts by weight of an activator, 1 part by weight of dimethyl polysiloxane (with a viscosity of 100 cSt. 20°C.) and 80 parts by weight of toluylene diisocyanate, which contains the isomers toluylene - 2,4- diisocyanate and toluylene - 2,6 - diisocyanate in the ratio 65 : 35. The activator is produced from a linear polypropylene glycol ether having a hydroxyl number of 92, which contains 2.46 parts by weight of sodium combined as alcoholate per 100 parts by weight of polypropylene glycol ether. The mixture of the components immediately becomes creamy and begins to foam with evolution of heat. After about 1½ minutes, the foaming is completed and after about 4 minutes the surface of the foam material is non-tacky. After cooling, a fine-pored, semi-rigid somewhat yellowish-coloured foam material with good resistance to abrasion and a bulk density of 88 kg/m³ is formed. The foam material can be cut, sawn and worked with cutting tools. Index: 885.

EXAMPLE 2

Production of the initial material:

7202 Parts by weight of a linear polypropylene glycol ether with a hydroxyl number of 92 are heated to a temperature of 200 to 205°C., with 1752 parts by weight of adipic acid for 20 hours while constantly stirring the reaction mixture. The heating during the last eight hours is performed in a vacuum of 12 mm. Hg., whereby 216 parts by weight of water are split off. After cooling, free adipic acid precipitates from the viscous reaction product and this is separated off. The somewhat brownish filtrate has an acid number of 47.9, a hydroxyl number of 1.7 and a viscosity of 205 cP/75°C. and of 2480 cP/25°C.

24.2 Ml. of aqueous caustic potash (2.6N) are added while stirring to 500 parts by weight of this polypropylene glycol ether dicarboxylic acid, and then it is dehydrated at 100°C. under a vacuum of 12 mm. Hg.

To 100 parts by weight of this potassium salt of polypropylene glycol ether dicarboxylic acid are added 1 part by weight of dimethyl polysiloxane (with a viscosity of 100 cSt 20°C) and 75 parts by weight of toluylene diisocyanate containing the isomers toluylene-2,4 - diisocyanate and toluylene - 2,6-diisocyanate in the ratio 65:35. After thoroughly mixing the components, the mass immediately foams and solidifies after about 5 minutes to form a rigid abrasion-resisting foam material which is somewhat brownish in colour and has a bulk density of 73 kg/m³. The foam material has largely open pored and does not show any shrinkage even after being boiled for several hours in water.

The amount of isocyanate used is calculated as follows:

7.70 parts by weight of toluylene diisocyanate are required for 100 parts by weight of polypropylene glycol ether dicarboxylic acid and 67.30 parts by weight of toluylene diisocyanate are required for cyclisation and side reactions so that 75.00 parts by weight of toluylene diisocyanate is required in all. Index: 974.

EXAMPLE 3

18.3 Ml. of aqueous 4.4N caustic potash solution are added while stirring to 500 parts by weight of the polypropylene glycol ether dicarboxylic acid described in Example 2 and then dehydration is carried out at 100°C. in a vacuum of 12 mm. Hg.

To 100 parts by weight of the above combination are added 1 part by weight of dimethyl polysiloxane (with a viscosity of 100 cSt. 20°C) 0.5 part by weight of permethylated diethylene triamine and 60 parts by weight of toluylene diisocyanate containing the isomers toluylene - 2,4- and toluene - 2,6-diisocyanates in the ratio 80 : 20. After mixing the components with a high speed stirrer, the mass immediately foams and solidifies in the course of a few minutes to form a semi-rigid foam material having the bulk density 65 kg/m³. In contrast to a foam material which has been produced without any permethylated diethylene triamine, the foam material has a pure white colour. Index: 780.

Using the same combination of substances as previously described, but with introduction of only 40 parts by weight of toluylene diisocyanate, a soft foam material with a bulk density of 60 kg/m³ is obtained. In this case, a clearly slower setting process is observed. The foam material shows no shrinkage on cooling or on boiling in water.

In the case where only 40 parts by weight of toluylene diisocyanate are used, an index of 520 is calculated.

EXAMPLE 4

22.5 Ml. of aqueous 4.4N caustic potash solution are added to 500 parts by weight of the polypropylene glycol ether dicarboxylic acid described in Example 2 while stirring, and then dehydrated at 100°C. in a vacuum of 12mm. Hg.

To 100 parts by weight of the above combination are added 15 parts by weight of dimerised linoleic fatty acid, (acid number 190), 1 part by weight of dimethyl polysiloxane (with a viscosity of 100 cSt. 20°C), 0.5 part by weight of permethylated diethylene

triamine and 80 parts by weight of toluylene diisocyanate containing the isomers toluylene-2,4- and toluylene - 2,6 - diisocyanates in the ratio 65 : 35. After mixing the components, the mass starts to foam and solidifies to form a rigid foam material with the bulk density of 25 kg/m³. In spite of its low bulk density, this foam material is distinguished by a good resistance to abrasion. The pores thereof are largely opened. Index: 660.

EXAMPLE 5

Production of the initial material:

1022 Parts by weight of adipic acid are esterified with 636 parts by weight of diethylene glycol over a period of 15 hours at 220°C., finally in a vacuum of 12 mm. Hg., and 215 parts by weight of water are split off. The resulting polyester has an acid number of 82, a hydroxyl number of 5 and a viscosity of 413 cP/75°C.

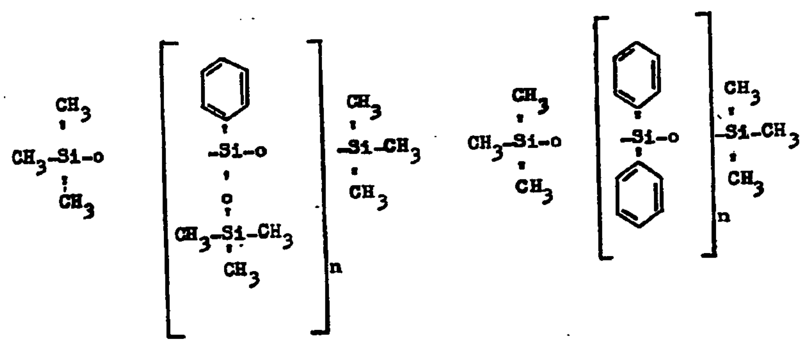
To produce a foam material, 80 parts by weight of the polyester are thoroughly mixed with 20 parts by weight of activator, (consisting of a mixture of potassium oleate in oleic acid with the acid number 130), 1 part by weight of permethylated diethylene triamine, as well as 80 parts by weight of toluylene diisocyanate containing the isomers toluylene - 2,4- and toluylene - 2,6 - diisocyanates in the ratio 65 : 35. The mixture of the components foams slowly with formation of a rigid foam material with a natural sponge structure. Bulk density 36 kg./m³. Index: 470.

EXAMPLE 6

Production of the initial material:

1200 Parts by weight of a polypropylene glycol ether (molecular weight 1200) are esterified with 219 parts by weight of adipic acid and 300 parts by weight of dimerised linoleic fatty acid in the course of 16 hours at 200°C., finally in a vacuum of 12 mm. Hg. Free adipic acid is deposited on the vessel walls which have not been contacted by the reaction mass, but the reaction material on the other hand shows no depositions of crystalline adipic acid. The acid number is 46.2, OH number is 2.6 and it has a viscosity of 322 cP/75°C. and 4200 cP/25°C.

To produce a foam material, 80 parts by weight of the reaction material are thoroughly mixed with 20 parts by weight of potassium oleate in oleic acid as activator, (acid number 130), 0.5 part by weight of permethylated ethylene diamine, 0.2 part by weight of a mixture of a branched and a linear homologous polymeric phenylmethyl polysiloxane of the formulae:



as well as 80 parts by weight of toluylene diisocyanate containing the isomers toluylene-2,4- and toluylene - 2,6 - diisocyanate in the ratio 65 : 35. The mixture of the components immediately becomes creamy, starts to foam and solidifies in the course of 2 minutes to provide a fine-pored semi-rigid foam material with the bulk density of 34 kg/m³.

EXAMPLE 7

Production of the initial material:

1800 Parts by weight of polyethylene glycol (molecular weight 600) are condensed with 584 parts by weight of adipic acid in the course of 15 hours at 200 to 205°C. under normal pressure, (108 parts by weight of water being split off), to provide a polyester with the acid number 48, and OH number 1.2 and a viscosity of 583 cP/75°C. and of 6380 cP/25°C.

A foam material is obtained from this polyester if 90 parts by weight thereof are thoroughly and quickly mixed with 10 parts by weight of potassium oleate in oleic acid (acid number of the combination 130), 1 part by weight of dimethyl benzylamine and 80 parts by weight of toluylene diisocyanate containing the isomers toluylene - 2,4- and toluylene - 2,6 - diisocyanate in the ratio 65 : 35. The mixture of the components becomes creamy, starts to foam and solidifies in the course of 1 minute into a semi-rigid foam material having the bulk density of 42 kg/m³. The foam material shows a slight degree of shrinkage after cooling. Index: 800.

EXAMPLE 8

Production of the initial material:

1200 parts by weight of dimerised linoleic fatty acid (acid number 190) are condensed with 600 parts by weight of polyethylene glycol (molecular weight 600) in 20 hours at 200 to 205°C. (36 parts by weight of water being split off), to provide a polyester (acid number 64, OH number 0, viscosity 710 cP/75°C. and 12550 cP/25°C.).

A foam material is obtained from this polyester if 88 parts by weight thereof are mixed with 12 parts by weight of potassium oleate in oleic acid, (acid number of the combination 130), 0.5 part by weight of permethylated tetramethylene diamine, 0.1 part by weight of the phenyl methyl polysiloxane described in Example 6, as well as 100 parts by weight of toluylene - diisocyanate containing the isomers toluylene - 2,4- and toluylene - 2,6-diisocyanates in the ratio 80 : 20. There is immediately formed a very creamy reaction mixture which starts to foam and which solidifies in the course of 1 minute into a fine-pored semi-elastic foam material with the bulk density of 35 kg/m³. This material has a relatively high number of closed pores, which results in a certain degree of shrinkage of the foam material after cooling to room temperature. Index: 803.

EXAMPLE 9

Production of the initial material:

To 1000 Parts by weight of dimerised linoleic fatty acid (acid number 190) are added while stirring 30 ml. of a substantially 50% aqueous caustic potash solution at room temperature and the mixture thereafter is dehydrated at 100°C. under reduced pressure. The reaction product, containing the potassium salt of the polycarboxylic acid dissolved in the said polycarboxylic acid, has an acid number of 167.

To produce a foam material, 100 parts by weight of the acid containing potassium salt are mixed with 0.5 part of weight of permethylated diethylene triamine, 0.2 part by weight of the phenylmethyl polysiloxane described in Example 6 and 80 parts by weight of toluylene diisocyanate containing the isomers toluylene - 2,4- and toluylene - 2,6 - diisocyanates in the ratio 65 : 35. The homogenised mixture of the components is solidified in the course of 8 minutes to give a rigid, fine-pored, very brittle foam material with the bulk density of 45 kg/m³. Index: 271.

With otherwise the same foam recipe, but working with 160 parts by weight of toluylene diisocyanate (*i.e.* with an index of 542), a likewise rigid and extremely brittle foam material having the bulk density 18 kg/m³ is obtained with a strong positive heat of reaction.

EXAMPLE 10

Production of the initial material:

1314 Parts by weight of adipic acid are condensed at 200 to 205°C with 821 parts by weight of diethylene glycol and 22.4 parts by weight of trimethylol propane under normal pressure in the course of 15 hours to give a polyester (acid number 80.2, hydroxyl number 1.8, viscosity 327 cP/75°C. and 5870 cP/25°C.).

A foam material is obtained from this polyester if 70 parts by weight thereof are mixed with 30 parts by weight of potassium oleate in oleic acid, (acid number of the activator combination is 130), 1 part by weight of silicone oil and 80 parts by weight of toluylene-2,4 - diisocyanate. The mixture foams and solidifies in the course of 2 minutes into a rigid foam material with a bulk density of 34 kg/m³. Index: 450.

EXAMPLE 11

Production of the initial material:

2000 Parts by weight of linear polypropylene glycol ether (hydroxyl number 56), 197 parts by weight of adipic acid and 390 parts by weight of a polyfunctional carboxylic acid (molecular weight 600, acid number 190 and obtained by polymerisation of unsaturated linoleic fatty acid) are esterified at 200 to 205°C. in the course of 12 hours, (the last six hours under a reduced pressure of 150 mm. Hg.), and 36 parts by weight of water are split off. The polyester obtained in this way has an acid number of 52, a hydroxyl number of 9 a viscosity of 275 cP/75°C. and of 3340 cP/25°C.

For the production of a foam material from this polyester, 75 parts by weight thereof are thoroughly mixed with 25 parts by weight of an activator combination consisting of a mixture of the potassium salt of polymerised linoleic fatty acid dissolved in the same linoleic fatty acid, (acid number of the combination 127), 0.5 part by weight of permethylated diethylene triamine, 0.2 part by weight of the phenylmethyl polysiloxane described in Example 6, as well as 100 parts by weight of toluylene diisocyanate containing the isomers toluylene - 2,4 - diisocyanate and toluylene - 2,6 - diisocyanate in the ratio 65 : 35. The mass immediately begins to foam and solidifies in the course of 90 seconds into a semi-rigid fine-pored foam material with a bulk density of 40 kg/m³. Index: 690.

In order to produce a foam material having a lower bulk density of 29 kg/m³ while using the same foam recipe, 1.5 parts by weight of water are concurrently employed. Index: 345.

A similar foam material is obtained if the activator used is the salt of a quaternary ammonium base with a carboxylic acid, obtainable by neutralisation of dibenzyl dimethyl ammonium hydroxide, (62.4% in water), with an excess of polymerised linoleic fatty acid, the acid number of the anhydrous combina-

tion being 153. The foam constituents are as follows:

60 Parts by weight of polyester as described above,

40 Parts by weight of quaternary ammonium salt,

0.5 Part by weight of permethylated diethylene triamine,

0.5 Part by weight of the organic silicone compound described in Example 12 and

100 Parts by weight of toluylene - diisocyanate, the same isomer ratio as above.

The foam material has a bulk density of 32 kg/m³.

EXAMPLE 12

60 Parts by weight of the polyester described in Example 11 are thoroughly mixed with 40 parts by weight of an activator combination consisting of a solution of the potassium salt of polymerised fatty acid of linseed oil in the same acid, (acid number of the combination 127), 1 part by weight of a copolymer of a trialkoxy polysiloxane and a polyethylene propylene glycol monoalkyl ether according to Example 1a of United Kingdom Patent Specification No. 804,369, as well as 140 parts by weight of a 90% solution of 4,4' - diphenylmethane - diisocyanate in chlorobenzene. The mass immediately becomes of a creamy consistency and starts to foam, solidifying in the course of 2½ minutes into a rigid foam material with a very uniform pore structure without any sign of shrinkage. Bulk density 50 kg/m³. Index: 501.

By the additional use of 1 part by weight of water and 140 parts by weight of 4,4'-diphenylmethane - diisocyanate (90% in trichlorodiphenyl) to the above foam constituents, a foam material of similar type is obtained, but with a bulk density of 32 kg/m³. Index: 323.

EXAMPLE 13

Preparation of the initial material:

A polyester is prepared by a known method from 1200 parts by weight of linear polypropylene glycol ether (molecular weight 1200), 260 parts by weight of adipic acid, 300 parts by weight of polymerised fatty acid of linseed oil (molecular weight 600, acid number 190) and 25 parts by weight of trimethylol propane. The polyester has an acid number of 55.8, a hydroxyl number of 1.5 and a viscosity of 373 cP/75°C. and of 5016 cP/25°C.

For the production of a foam material, 65 parts by weight of this polyester are intimately mixed with 35 parts by weight of potassium salt of polymerised fatty acid in the same acid, (acid number of the combination 157), 0.3 part by weight of the phenylmethyl polysiloxane described in Example 6, 0.5 part by weight of permethylated hexamethylene diamine as well as 80 parts by weight of toluylene - diisocyanate, containing the isomers toluylene - 2,4-diisocyanate and toluylene - 2,6 - diisocyanate in the ratio 80 : 20. A rigid foam material with a fine pore structure is formed with a bulk density of 30 kg/m³. The foam material already has a dry surface after 1½ minutes setting time and can be cut after another 10 minutes. Index: 497.

EXAMPLE 14

60 Parts by weight of a branched polypropylene glycol ether (obtained by adding propylene oxide to trimethylol propane) and having a hydroxyl number of 56 are thoroughly mixed with 40 parts by weight of an activator combination comprising the potassium salt of polymerised fatty acid of linseed oil, dissolved in the same acid, (acid number of the combination 167), one part by weight of the organic silicon compound described in Example 12, 0.5 part by weight of permethylated diethylene triamine, 2 parts by weight of water and also 100 parts by weight of toluylene - diisocyanate, (isomer ratio between toluylene - 2,4 - diisocyanate and toluylene - 2,6 - diisocyanate 65 : 35). The mixture of the components starts to foam and solidifies after two minutes into a fine-pored semi-rigid foam material with a bulk density 29.5 kg/m³. Index: 275.

A soft foam material with a bulk density of 39 kg/m³ is obtained by combining the following:

60 Parts by weight of branched polypropylene glycol ether,

40 Parts by weight of activator combination,

1 Part by weight of the above organic silicon compound,

2 Parts by weight of water,

0.5 Part of weight of permethylated diethylene triamine and

40 Parts by weight of toluylene - diisocyanate, (isomer ratio as above).

The mixture of the components expands over a period of 3 minutes into a foam material which is surface-dry after 15 minutes. Index of this composition is 235.

EXAMPLE 15

60 Parts by weight of a linear polypropylene glycol ether (hydroxyl number 150) are thoroughly mixed with 40 parts by weight of an activator combination consisting of the potassium salt of polymerised fatty acid of linseed oil dissolved in the same acid, (acid number of the combination 167), 1 part by weight of the organic silicon compound described in Example 12, as well as 60 parts by weight of toluylene - diisocyanate, the ratio between the isomers of toluylene - 2,4- and toluylene - 2,6 - diisocyanates being 80 : 20. The mixture of the components foams and solidifies within 2 minutes into a surface-dry, fine-pored, rigid foam material with a bulk of density 32 kg/m³. Index: 233.

EXAMPLE 16

60 Parts of weight of a branched polypropylene glycol ether (hydroxyl number 270), obtained by addition of propylene oxide to trimethylol propane, are thoroughly mixed with 40 parts by weight of an activator combination consisting of the potassium salt of polymerised fatty acid of linseed oil, dissolved in the same acid, (acid number of the combination 167), 1 part by weight of the organic silicon compound described in Example 12, 0.5 part by weight of permethylated ethylene diamine, as well as 100 parts by weight of toluylene - diisocyanate, the ratio between the isomers of toluylene - 2,4- and toluylene-2,6 - diisocyanates being 65 : 35. The creamy reaction mixture very quickly starts to foam and solidifies after 30 seconds into a surface-dry rigid foam material with a bulk density 29 kg/m³. Index: 270.

EXAMPLE 17

90 Parts by weight of a linear polypropylene glycol ether (hydroxyl number 56), obtained by polymerising propylene oxide, are thoroughly mixed with 10 parts by weight of a sodium alcoholate solution of linear polypropylene glycol ether of the molecular weight 1200, (containing 2.46 g. of sodium), 100 g. of polypropylene glycol ether, 0.5 part by weight of the organic silicon compound described in Example 12, 2 parts by weight of water and 100 parts by weight of toluylene-diisocyanate, (isomer ratio 65 : 35). The mixture solidifies with foaming in the course of 1 minute to provide a fine-pored rigid foam material with the bulk density 54 kg/m³. Index: 349.

A similar foam material is obtained with the use of a branched polypropylene glycol ether (hydroxyl number 56) obtained by addition of propylene oxide to trimethylol propane, the foam being made from:

95 Parts by weight of branched polypropylene glycol ether

5 Parts by weight of activator as above

0.1 Part by weight of an organic silicon compound according to Example 12

3 Parts by weight of water and

100 Parts by weight of toluylene - diisocyanate.

The foam material has a bulk density of 38 kg/m³. Index: 263.

EXAMPLE 18

Components	Experiment No. 1	2	3	4	5	6	7
	giving amounts of each component in parts by weight						
A	70	70	70	70	70	85	85
B	30	30	30	30	30	—	—
C	—	—	—	—	—	15	15
D	0.5	0.5	0.5	0.5	0.5	0.5	0.5
E	100	—	—	100	100	100	120
F	—	100	—	—	—	—	—
G	—	—	140	—	—	—	—

In the above Table:

A represents a branched polypropylene glycol ether (3.2% OH, viscosity 397 cP/25° C.), obtained by addition of propylene oxide to xylitol.

B represents the potassium salt of polymerised fatty acid of linseed oil dissolved in the same acid, (acid number of combination 167).

C represents a linear polypropylene glycol ether, (hydroxyl number 56), with 0.87 part by weight of sodium combined as alcoholate per 100 parts by weight of polypropylene glycol ether.

D represents an organic silicon compound according to Example 12.

E represents toluylene-diisocyanate, (isomer ratio 80:20).

F represents toluylene-2,4-diisocyanate.

G represents 4,4¹-diphenylmethane-diisocyanate, 90% in chlorobenzene.

The foaming reaction starts immediately on mixing the components. With rising times of about 2 minutes, the result is surface-dry rigid foam materials with the following bulk densities and indices:

	1	2	3	4	5	6	7
Bulk density kg/m^3	28	58	61	31	31	69	47
Index	256	492	431	334	252	336	304

EXAMPLE 19

70 Parts by weight of castor oil are mixed with 30 parts by weight of potassium oleate in oleic acid, (acid number of the activator combination 130), 0.2 part by weight of the organic silicon compound described in Example 12 and 120 parts by weight of toluylene - 2,4 - diisocyanate. In a moderate reaction a fine-pored foam material which has a dry surface after about 14 minutes is formed. The rigid and brittle foam material has a bulk density of 45 kg/m^3. Index: 415.

EXAMPLE 20

Using the working procedure described in United Kingdom Patent Application No. 39032/58 (Serial No. 888,691), an initial adduct-containing isocyanate (NCO content 10.4%, viscosity 7290 cP/25°C) is prepared from 70 parts by weight of linear polypropylene glycol ether (hydroxyl number 56) and 29 parts altogether by weight of toluylene-diisocyanate, (isomer ratio 65 : 35). 100 Parts by weight of this initial adduct are mixed with 40 parts by weight of toluylene-diisocyanate, isomer ratio as above and now yield an isocyanate-containing initial adduct with an NCO content of 21.2%.

For the production of a foam material, 80 parts by weight of the previously described initial adduct containing isocyanate groups are quickly and thoroughly mixed with 0.12 part by weight of the organic silicon compound described in Example 12 and with 20 parts by weight of an activator combination of the potassium salt of the polymerised fatty acid of linseed oil dissolved in the same acid, (acid number of the combination 167). The reaction mixture foams immediately and solidifies directly afterwards into a semi-elastic foam material with the bulk density 30. Index: 606.

EXAMPLE 21

70 Parts by weight of a polybutylene glycol ether (hydroxyl number 94.6, viscosity 20.1 cP/75°C. and 206 cP/25°C) are mixed with 30 parts by weight of an activator combination of the potassium salt of polymerised fatty acid of linseed oil dissolved in the same acid, (acid number of the combination 157), 0.2 part by weight of the organic silicon compound described in Example 12 and 100 parts by weight of toluylene - 2,4 - diisocyanate. The reaction mass starts to foam and solidifies after a rising time of 1½ minutes into a fine-pored semi-rigid foam material with a bulk density of 40 kg/m^3. Index: 522.

A similar foam material with a bulk density of 27 kg/m^3 is obtained by mixing together 70 parts by weight of the polybutylene glycol ether as described in this Example, 30 parts by weight of a polymeric linoleic acid (molecular weight 600, acid number 190), 1 part by weight of permethylated diethylene triamine, 0.5 part by weight of the organic silicon compound described in Example 12, 7 parts by weight of a 17% potassium hydroxide solution in a 3:1 mixture of benzyl alcohol and methyl alcohol and 100 parts by weight of toluylene - diisocyanate, (ratio between toluylene - 2,4 - diisocyanate and toluylene-2,6 - diisocyanate 65 : 35). The index of this combination is calculated as 375.

EXAMPLE 22

70 Parts by weight of a branched polypropylene glycol ether (hydroxyl number 56) obtained by adding propylene oxide to trimethylol propane are mixed with 30 parts by weight of polymerised fatty acid of linseed oil (molecular weight 600, acid number 190), 5 parts by weight of permethylated diethylene triamine, 0.2 part by weight of the organic silicon compound described in Example 12, 5 parts by weight of methyl alcohol and 80 parts by weight of toluylene - 2,4 - diisocyanate. The reaction mass starts to foam and solidifies in 2½ minutes to form a rigid foam material with the bulk density 44 kg/m^3. Index: 280.

A similar foam material is obtained if the methyl alcohol is replaced by the substituted carbamic acid methyl ester obtained from toluylene-2,4-diisocyanate and methyl alcohol. The foaming process is made slower and the bulk density of the foam material is 89 kg/m^3.

EXAMPLE 23

100 Parts by weight of the polyester described in Example 11 are mixed with 10 parts by weight of zinc stearate, 5 parts by weight of permethylated diethylene triamine, 0.5 part by weight of the organic silicon compound described in Example 12

and 80 parts by weight of toluylene - 2,4-diisocyanate. In a moderate reaction, a coarse-pored foam material is formed within 10 minutes with expansion of the reaction mixture. Bulk density 69 kg/m^3. Index: 845.

EXAMPLE 24

80 Parts by weight of polyester according to Example 11, 20 parts by weight of polymerised fatty acid of linseed oil, (molecular weight 600, acid number 190), 20 parts by weight of sodium 4 - chloro - 2 - nitrophenyl, 0.2 part by weight of organic silicon compound according to Example 12, 100 parts by weight of toluylene - diisocyanate, (isomer ratio 80 : 20), are homogeneously mixed. In a quick reaction, a semi-rigid foam material is formed with a bulk density of 24 kg/m^3, this material being yellowish in colour after storage. Index: 741.

EXAMPLE 25

60 Parts by weight of a branched polypropylene glycol ether (hydroxyl number 56) obtained by addition of propylene oxide to trimethylol propane are mixed with 40 parts by weight of an activator combination consisting of the potassium salt of the polymerised fatty acid of linseed oil dissolved in the same acid, (acid number of the combination 167), 2 parts by weight of permethylated diethylene triamine, 0.5 part by weight of the silicon compound described in Example 12 and 120 parts by weight of 4,4^1 - diphenyl methane diisocyanate, 90% in chlorobenzene. The reaction mass starts to rise and solidifies in a period of 2 minutes to form a fine-pored rigid foam material with a bulk density of 47.5 kg/m^3. Index: 441.

A similar foam material with a bulk density of 46 kg/m^3 is obtained by using a linear polypropylene glycol ether of the same hydroxyl number instead of the aforesaid branched type.

EXAMPLE 26

30 Parts by weight of the polyester described in Example 11 are mixed with 20 parts by weight of an activator combination consisting of the potassium salt of the polymerised fatty acid of linseed oil in the same acid, (acid number of combination 127), 1 part by weight of permethylated diethylene triamine and 0.2 part by weight of organic silicon compound according to Example 12 and heated to a temperature of 70°C. To this mixture are added 150 parts by weight of a 75% ethyl acetate solution of the polyisocyanate referred to below (NCO content 14%), the said solution being preheated to the same temperature. After mixing all the reaction components, the mixture starts to foam and solidifies in a period of 10 minutes into a rigid foam material with the bulk density of 44.5 kg/m^3. The polyisocyanate is obtained by reacting 1 mol of trimethylol propane with 3 mols of toluylene - 2,4 - diisocyanate.

EXAMPLE 27

100 Parts by weight of a mixture of 60 parts by weight of a linear polypropylene glycol ether (hydroxyl number 56) and 40 parts by weight of a polycarboxylic acid (acid numebr 190) obtained by polymerisation of fatty acid of linseed oil and 0.3 part by weight of the organic silicon compound described in Example 12 (this mixture being designated as component I) are mechanically homogenised at normal temperature with 6 parts by weight of an activator mixture consisting of 16.7% of potassium hydroxide, 16.7% of permethylated diethylene triamine and 66.6% of methyl alcohol (component II), the homogenisation being obtained by injecting component II into the flowing stream of component I. The further mixing of the resulting mixture of components I and II with 100 parts by weight of toluylene - diisocyanate, (2,4- to 2,6- isomer ratio 80 : 20), takes place at room temperature by injection of the toluylene - diisocyanate into the flowing steam of the combination consisting of I and II. The reactive mixture obtained by a mixing time of about 1/300 of a second is initially a fairly clear liquid, which starts to foam after about 3 to 5 seconds and has solidified in a period of about 20 to 30 seconds into a semi-rigid foam material (bulk density 21 kg/m^3). The foam material has a dry surface. After cooling, it can be sawn, cut or machined in any other way. This combination is especially suitable for insulation purposes and existing cavities can be satisfactorily filled therewith.

EXAMPLE 28

70 Parts by weight of a linear polyether (hydroxyl number 56) obtained by addition of propylene oxide to polyethylene glycol (molecular weight 300) are mixed with 30 parts by weight of an activator combination consisting of the potassium salt of polymerised fatty acid of linseed oil, dissolved in the same acid, (acid number of the combination 165), 0.5 part by weight of the organic silicon compound described in Example 12 and 100 parts by weight of toluylene - diisocyanate (isomer ratio between toluylene - 2,4- and toluylene - 2,6- diisocyanates being 65 : 35). The mixture starts to foam and solidifies into a semi-rigid fine-pored foam material with a bulk density of 32.6 kg/m^3. After 1 minute, calculated from the time of mixing the components the foam material already shows a surface which is no longer tacky.

Example 29

Components	Experiment No. 1	2	3	4	5
	giving amounts of each component in parts by weight				
A	60	50	40	20	—
B	—	—	—	—	100
C	—	—	—	80	—
D	40	50	60	—	—
E	150	150	150	100	100
F	0.5	0.5	0.5	0.5	0.5
H_2O	—	—	—	2.0	2.0
Bulk density Kg/m³	35	30	32	54	44
Index	379	395	415	281	255

A: A branched polyether (molecular weight 750, OH number 298) obtained by adding ethylene oxide (45%) and propylene oxide (55%) to ethylene diamine.

B: Polyether as in A (molecular weight 1750, OH number 128).

C: A linear polypropylene glycol ether (molecular weight 2000, OH number 56).

D: A polycarboxylic acid obtained by polymerisation of fatty acid of linseed oil (molecular weight 600).

E: Toluylene-diisocyanate which contains the isomers toluylene-2,4-diisocyanate and toluylene-2,6-diisocyanate in the ratio 65 : 35.

F: Organic silicon compounds mentioned in Example 12.

The components are mixed in the quantities indicated. The mixture immediately starts to foam. The reaction mass is solidified within 1—2 minutes to form a surface-dry, semi-elastic foam material.

Example 30

25 Parts by weight of a linear polypropylene glycol ether (molecular weight 2000, hydroxyl number 56) are mixed with 25 parts by weight of a dimerised linoleic acid (molecular weight 600), 50 parts by weight of a branched polyester (hydroxyl number 180) obtained from 1.4 mols of adipic acid, 1 mol of hexanetriol and 1 mol of 1,3 - butylene glycol, 2 parts by weight of a 17% potassium hydroxide solution in benzyl alcohol - methyl alcohol (3 : 1), 1 part by weight of permethylated aminoethylpiperazine, 0.3 part by weight of the organic silicon compound mentioned in Example 12 and 100 parts by weight of toluylene - diisocyanate, (mixing ratio between toluylene - 2,4- and toluylene-2,6 - diisocyanates 65 : 35). The creamy mixture of the components immediately starts to foam and is solidified in the course of 2 minutes into a rigid foam material (bulk density 30 kg/m³) of very uniform pore structure and good resistance to abrasion. Index: 389.

Example 31

60 Parts by weight of a polythioether (hydroxyl number 53) prepared from thiodiglycol and triethylene glycol in accordance with Example 2 of United Kingdom Patent Specification No. 832,352, are mixed with 40 parts by weight of a combination of the potassium salt of the polymerised fatty acid of linseed oil dissolved in the same acid, (acid number of combination 165), 1 part by weight of permethylated diethylene triamine, 0.5 part by weight of the organic silicon compound mentioned in Example 12 and 100 parts by

weight of toluylene - diisocyanate, (ratio between the isomers toluylene - 2,4- and toluylene - 2,6 - diisocyanates, 65 : 35). The reaction mixture immediately becomes creamy, starts to foam and is solidified after 2 minutes into a rigid fine-pored foam material (bulk density 30 kg/m^3). Index: 596.

EXAMPLE 32

Production of the initial material:

In a stainless steel stirrer-type vessel having tin plates secured to the stirrer and a total weight of 160 parts by weight, 5110 parts by weight of adipic acid, 4178 parts by weight of diethylene glycol and 52 parts by weight of trimethylol propane are heated for 23 hours to 200°C. (the last 5 hours under a vacuum of 15 mm. Hg.). During this time 1260 parts by weight of water are split off with formation of a polyester (acid number 1.3, hydroxyl number 75, viscosity 6250 cP/25°C., content of dissolved tin 0.008%).

A foam material is obtained from this branched polyester by mixing 100 parts by weight thereof with 2 parts by weight of water, 0.5 part by weight of the organic silicon compound described in Example 12, 3 parts by weight of a 17% potassium hydroxide solution in a benzyl alcohol-methyl alcohol mixture (3 : 1) and 100 parts by weight of toluylene - diisocyanate, (ratio between toluylene - 2,4- and toluylene - 2,6-diisocyanates, 80 : 20). Directly after combining the components, the mixture starts to foam and solidifies into a rigid foam material (bulk density 23 kg/m^3). Index: 380.

EXAMPLE 33

Production of the starting material:

1660 Parts by weight of a linear polypropylene glycol ether (molecular weight 415, hydroxyl number 270) obtained by polymerisation of propylene oxide are esterified with 730 parts by weight of adipic acid at 200°C. over a period of 19 hours to form a polyester (acid number 56, hydroxyl number 17, viscosity 3190 cP/25°C.).

For the preparation of a foam material, 100 parts by weight of this polyester are mixed with 0.3 part by weight of the organic silicon compound described in Example 12, 5 parts by weight of a 17% potassium hydroxide solution in benzyl alcohol - methyl alcohol (3 : 1) and 100 parts by weight of toluylene-2,4 - diisocyanate. The mixture immediately starts to foam and solidifies in the course of 2 minutes into a non-shrinking rigid foam material (bulk density 28 kg/m^3). Index: 600.

Example 34

Components	Experiment No. 1	2	3
	giving amounts of each component in parts by weight		
A	100	70	—
B	—	—	100
C	—	30	—
D	100	100	100
E	0.5	0.5	0.5
F	3	6	6
G	1	1	—
Index	840	469	322
Bulk density kg/m^3	62	25.5	25

A: The compound obtained by addition of 1 mol of hexahydrophthalic acid anhydride to 1 mol of a linear polypropylene glycol ether (molecular weight 2000); the adduct has an acid number 28, OH number 28 and viscosity 90 cP/75° C.

B: The compound obtained by addition of 0.75 mol of hexahydrophthalic acid anhydride to 1 mol of polybutylene glycol (molecular weight 580); the adduct has an acid number 62, hydroxyl number 97 and viscosity 1293 cP/25° C.

C: The polycarboxylic acid (molecular weight 600, acid number 190) obtained by polymerisation of linoleic acid.

D: A mixture of the toluylene-2,4-diisocyanate and toluylene-2,6-diisocyanate in the ratio 65 : 35.

E: An organic silicon compound mentioned in Example 12.

F: 17% Potassium hydroxide solution in benzyl alcohol-methyl alcohol (3 : 1).

G: Permethylated diethylene triamine.

If the components are combined in the proportions indicated, the homogenised mixture starts to foam and solidifies into fine-pored rigid foam materials which are excellently suitable for insulation purposes.

Example 35

100 Parts by weight of component A are mixed with 100 parts by weight of toluylene-diisocyanate, (isomer ratio 65 : 35), and 2 parts by weight of a 17% potassium-hydroxide solution in benzyl alcohol - methyl alcohol (3 : 1) with the parts by weight of the blowing agents A-I as indicated below. In all cases, the reaction mixtures immediately foam after the components have been stirred together and solidify in the course of 1—2 minutes into rigid foam materials with the bulk densities as indicated. The foam materials A-D and H show a pure-white core, while the remainder have more or less strong brownish-coloured core discolourations. All foam materials have a uniformly fine pore structure. The component A is a mixture of 70 parts by weight of a polyester of 3 mols of polypropylene glycol (OH number 270) and 2 mols of adipic acid (acid number 2,

OH number 84), 30 parts by weight of a polyester of 2 mols of phthalic acid anhydride, 1 mol of adipic acid, 1 mol of oleic acid and 5.3 mols of trimethylol propane (OH number 353, acid number 0.5), 1 part by weight of permethylated diethylene triamine and 0.3 part by weight of the organic silicon compound mentioned in Example 12. Index: 358.

Blowing Agent

A	Trichlorfluormethane	20 parts by weight	Bulk density 26 kg/m³
B	1,1-Dichlorethylene	13 „ „ „	„ „ 30 „
C	*n*-Propylchloride	11 „ „ „	„ „ 28 „
D	1,2-Dichlorethylene	13 „ „ „	„ „ 29 „
E	Trichlorethylene	19 „ „ „	„ „ 40 „
F	1,2-Dichloropropane	16 „ „ „	„ „ 38 „
G	Tetrachlormethane	20 „ „ „	„ „ 36 „
H	*n*-Butylchloride	13 „ „ „	„ „ 26 „
I	1,2-Dichlorethane	14 „ „ „	„ „ 35 „

EXAMPLE 36

Components	Experiment No. 1	2	3	4
	giving amounts of each component in parts by weight			
A	100	100	100	100
Anisol-2,4-diisocyanate	100	—	—	—
m-phenylene diisocyanate	—	100	—	—
p-Phenylene diisocyanate	—	—	100	—
Toluylene-2,4-diisocyanate	—	—	—	100
B	6	3	2	—
C	1	1	—	1
Potassium phthalimide	—	—	—	10
Bulk density of foam material kg/m³	23	24	33	38
Index	387	537	568	588

In the components mentioned in the above Table are mixed together, rigid foam materials with the bulk densities indicated are obtained after a setting time of a few minutes. The diisocyanates which are solid at room temperatures are melted down before being mixed with the other components.

In the Table:

A represents a mixture of 60 parts by weight of a linear polypropylene glycol ester (OH number 56), 40 parts by weight of dimerised linoleic acid (acid number 190) and 0.3 part by weight of the organic silicon compound mentioned in Example 12. Acid number of the mixture 78, viscosity 1240 cP/25°C.

B represents 17% potassium hydroxide solution in benzyl alcohol and methyl alcohol (3 : 1).

C represents permethylated diethylene triamine.

EXAMPLE 37

100 Parts by weight of a mixture of viscosity 1380 cP/25°C, of 80 parts by weight of a linear polypropylene glycol ether (OH number 93) and 20 parts by weight of a styrene - allyl alcohol copolymer (molecular weight 1150), (OH number 252), are mixed with 1 part by weight of 17% potassium hydroxide solution in benzyl alcohol and methyl alcohol (3 : 1), 0.3 part by weight of the organic silicon compound described in Example 12, 0.75 part by weight of permethylated diethylene triamine, 2.5 parts by weight of water and 100 parts by weight of toluylene - diisocyanate, (isomer ratio 65 : 35).

The mixture immediately becomes creamy and starts to foam with formation of a rigid foam material having a uniform and very fine pore structure (bulk density 36 kg/m^3). The foam material has particularly good resistance to abrasion. Index: 224.

WHAT WE CLAIM IS:—

1. A process for the production of foam materials which comprises reacting at least one polyhydroxyl and/or polycarboxyl compound with a molecular weight greater than 300 and, if necessary or if desired (the latter case being where carboxyl groups are present), a compound which produces a blowing action under the reaction conditions, in the presence of a catalyst capable of polymerising isocyanates to form a perhydrotriazine ring, with more than twice the quantity of polyisocyanate which is required for reaction with the free hydroxyl and/or carboxyl groups and, if present and reactive, the compound which produces a blowing action under the reaction conditions.

2. A modification of the process claimed in claim 1, wherein the polyhydroxyl and/or polycarboxyl compound is reacted in a first step with the polyisocyanate to form a prepolymer containing free NCO groups and this prepolymer is reacted in a second step with the compound which produces a blowing action under the reaction conditions.

3. A process as claimed in claim 1, wherein the catalyst capable of polymerising isocyanates to form a perhydrotriazine ring has an alkaline reaction in an aqueous medium.

4. A process as claimed in claim 3, wherein the catalyst is a compound of the general formula

$$R—O^{\ominus}Me^{\oplus}$$

in which, Me represents an alkali metal or a quaternary ammonium group and R represents a hydrogen atom or an alkyl, aryl, aralkyl or cycloalkyl group.

5. A process as claimed in claim 3, wherein the catalyst is a tertiary amine.

6. A process as claimed in any of the preceding claims, wherein the compound which produces a blowing action under the reaction conditions is water.

7. A process as claimed in any of the preceding claims, wherein the polyhydroxyl compound is a polyalkylene glycol ether.

8. A process as claimed in claim 7, wherein the polyalkylene glycol ether has a molecular weight between 300 and 10,000.

9. A process as claimed in any of the preceding claims, wherein the polyisocyanate is toluylene - 2,4 - diisocyanate or toluylene-2,6 - diisocyanate or a mixture thereof.

10. A process as claimed in any of the preceding claims, wherein the hydroxyl and/or carboxyl group containing compound is a polyether or polyester containing a polymerisable double bond.

11. A process as claimed in any of the preceding claims, wherein the amount of polyisocyanate used is such that the isocyanate index, as hereinbefore defined, is from 500 to 1000.

12. A process as claimed in any of the preceding claims, wherein the blowing action is supplemented by introducing air, carbon dioxide or nitrogen into the reaction mixture.

13. A process as claimed in any of the preceding claims, substantially is described with reference to any one of the Examples.

14. Foam materials when produced by a process as claimed in any one of the preceding claims.

ELKINGTON AND FIFE,
Chartered Patent Agents,
Bank Chambers, 329 High Holborn,
London, W.C.1.
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1962. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

6

RÉPUBLIQUE FRANÇAISE

MINISTÈRE DE L'INDUSTRIE

SERVICE
de la PROPRIÉTÉ INDUSTRIELLE

BREVET D'INVENTION

P.V. n° 860.836 — N° 1.289.074

Classification internationale : C 08 g

Procédé de préparation de produits mousse à base d'isocyanate.

Société dite : FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT résidant en République Fédérale Allemande.

Demandé le 5 mai 1961, à 12h 41m, à Paris.
Délivré par arrêté du 19 février 1962.
(*Bulletin officiel de la Propriété industrielle,* n° 13 de 1962.)
(*Demande de brevet déposée en République Fédérale Allemande le 6 mai 1960, sous le n° F 31.174, au nom de la demanderesse.*)

Il est connu de préparer suivant le procédé de polyaddition aux isocyanates, à partir de dérivés à poids moléculaire déjà élevé possédant des atomes d'hydrogène susceptibles de réagir et des polyisocyanates, des matières plastiques, auquel cas il se développe pendant la formation de la structure à poids moléculaire élevé, par un choix convenable des réactifs, du gaz carbonique qui fait gonfler la structure à poids moléculaire élevé en un produit mousse. Dans ce but, on est parti de dérivés à poids moléculaire élevé présentant des groupes carboxyles mais, industriellement, en particulier, on a préféré ajouter de l'eau aux matières premières contenant des groupes OH. Ce dernier procédé présente, du point de vue de l'utilisation des isocyanates, l'inconvénient d'être peu rationnel, étant donné qu'une molécule d'eau consomme deux groupes NCO.

En conséquence, on a déjà essayé de faire réagir des dérivés polyhydroxylés avec des polyisocyanates, en présence d'halogéno-alcanes, comme agents gonflants, en utilisant des quantités aussi petites d'eau, voire pas du tout, pour obtenir des produits mousse. Les produits mousse préparés suivant ce procédé, en particulier ceux pour lesquels on n'emploie pas d'eau, se différencient des produits mousse préparés avec de l'eau de la manière bien connue, cependant sans halogéno-alcanes, par une mollesse plus grande.

Sous ce rapport, on a préconisé de réaliser le processus de moussage exclusivement à l'aide d'halogéno-alcanes, auquel cas on doit opérer expressément en l'absence d'eau, mais aussi en l'absence de groupe carboxyle pour exclure totalement la formation de gaz carbonique.

L'objet de la présente invention est, en conséquence, un procédé pour la préparation de produits mousse à base d'isocyanate, à partir de dérivés polycarboxylés avec un poids moléculaire supérieur à 200, de polyisocyanates, d'activateurs et d'agents gonflants qui est caractérisé par le fait qu'on fait réagir les dérivés polycarboxylés avec un indice d'acide supérieur à 20 et un total de l'indice d'acide et de l'indice d'hydroxyle de 150-600 en l'absence d'eau avec, au maximum, le double de la quantité équivalente de polyisocyanate, en présence d'hydrocarbures halogénés insaturés et/ou saturés, avec un point d'ébullition inférieur à 150.

Dans ce procédé, l'action de gonflement se produit avec formation de mousse par réaction d'un groupe NCO avec un groupe COOH avec formation d'un groupe carbonamide et dégagement simultané de gaz carbonique. L'action de gonflement est favorisée par les hydrocarbures halogénés saturés et/ou insaturés. Ce mode opératoire présente, à beaucoup de points de vue, des avantages par rapport au procédé indiqué au début. Le fait que l'on n'emploie pas d'eau simplifie le cours de la réaction totale étant donné qu'il n'est plus nécessaire d'ajuster les réactions NCO-OH et NCO-H_2O dans le sens d'un déroulement synchrone, ce qui, on le sait, présente souvent des difficultés. Le procédé de la présente invention apporte ainsi, du fait de son mode opératoire plus simple, non seulement une plus grande sûreté de fabrication, mais, en outre, du fait d'une consommation plus faible en polyisocyanate, encore une économie.

Une différence essentielle du nouveau mode opératoire par rapport aux procédés où l'on travaille avec des dérivés polyhydroxylés et des halogéno-alcanes à l'exclusion d'eau, repose sur la présence des groupes carboxyles qui, au cours du moussage, se transforment, dans une mesure plus grande, pour engendrer des groupes carbonamides susceptibles de liaisons secondaires. Ce fait trouve une expression visible dans une autre propriété des mousses de carbonamide comparée à celles qui ne contiennent que des groupes uréthanes. Le procédé réunit donc

Prix du fascicule : 1 NF

les avantages des mousses isocyanate-eau, dans lesquelles il se forme également des groupes urées susceptibles de donner également des valences secondaires et des mousses d'uréthane pures, gonflées par les halogéno-alcanes qui se signalent par une grande économie du point de vue mise en œuvre des isocyanates.

Les dérivés polycarboxylés convenant pour le procédé présentent un poids moléculaire supérieur à 200 et un indice d'acide supérieur à 20. Ils peuvent encore comporter en outre des groupes hydroxyles, cependant, la somme des indices d'acide et d'hydroxyles se trouve dans l'intervalle 150-600. Sont à considérer comme exemples suivant le procédé de condensation bien connu des polyesters linéaires ou ramifiés obtenus à partir d'alcools, polyfonctionnels, aminoalcools, acides hydroxycarboxyliques, aminocarboxyliques, ou polycarboxyliques. Par l'ajustement des proportions de composants et aussi par le type de condensation, il est possible, facilement, de préparer des polyesters avec des groupes carboxyles ou aussi avec des groupes carboxyles et des groupes hydroxyles. Des dérivés convenables pour la préparation de tels polyesters sont par exemple l'éthylèneglycol, le diéthylèneglycol, ou les polyéthylèneglycols de formule générale :

$$HO\text{-}[CH_2\text{-}CH_2\text{-}O]\text{-}_nCH_2\text{-}CH_2\text{-}OH$$

dans laquelle n représente un nombre entier supérieur à 1, le propylèneglycol, le dipropylèneglycol ou les polypropylèneglycols de formule générale :

$$HO\text{-}[\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}O]\text{-}_nCH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}OH$$

auquel cas n représente un nombre entier supérieur à 1, des glycols de formule générale :

$$HO(CH_2)_nOH$$

dans laquelle n représente un nombre entier supérieur à 2, butanediol-1,3, butanediol-2,3, 2,2-diméthylpropanediol-1,3 butylène-2-diol-1,4, ou encore glycérine, triméthylol-propane, hexanetriol-1,2,6, pentaérythrite, sorbite, produits d'addition des oxydes d'alcoylène, comme les oxydes d'éthylène, de propylène, de 1,2- ou 2,3-butylène, de styrène, l'épychlorhydrine, le tétrahydrofurane sur des alcools di-et/ou poly-fonctionnels nommés, l'acide lactique, la butyrolactone, la caprolactone, l'acide ricinoléique, l'acide tartrique, l'acide citrique, l'acide oxalique, les acides alcoylène-dicarboxyliques de formule générale :

$$HOOC\text{-}[CH_2]\text{-}_nCOOH$$

dans laquelle n est un nombre entier supérieur à 0, les acides maléique ou fumarique, phtalique par polymérisation d'acides polycarboxyliques dimères ou avec une fonctionnalité supérieure obtenus par polymérisation d'acides gras insaturés, les acides polycarboxyliques obtenus par synthèse diénique avec par exemple l'anhydride maléique ou les produits d'hydrogénation de ceux-ci.

Par l'emploi simultané d'amino-alcools ou des polyamines ou des acides aminocarboxyliques avec des atomes d'azote tertiaire, on obtient également des polyesters-amides appropriés.

Les polyesters ou polyamides obtenus à partir des matières ci-dessus ou d'autres peuvent être modifiés avec des alcools ou des acides carboxyliques monofonctionnels comme par exemple des acides gras saturés ou insaturés. D'autres dérivés polycarboxylés convenables peuvent être obtenus par fixation d'anhydrides polycarboxyliques sur des composants linéaires ou ramifiés comportant des groupes hydroxyles comme par exemple polyesters, polyesters-amides, éthers ou thioéthers de polyalcoylèneglycol, polyacétals. Des anhydrides convenables sont, par exemple, les anhydrides maléique, succinique, phtalique, hexahydrophtalique, citraconique, pyromellitique, trimellitique ou aussi des produits d'addition de l'anhydride maléique sur l'hexachlorocyclopentadiène ou le produit d'hydrogénation de celui-ci.

On citera encore les produits obtenus par fixation de nitrile acrylique sur les dérivés polyhydroxylés comme par exemple les éthers linéaires ou ramifiés de polyalcoylèneglycols, l'amidon dégradé ou l'acétylcellulose avec saponification subséquente des produits d'addition. A la place du nitrile acrylique, on peut parfois faire agir directement l'acide acrylique.

On citera encore les acides polycarboxyliques-éthers de polyalcoylèneglycols obtenus par oxydation des éthers de polyalcoylèneglycol suivant le procédé du brevet allemand n° 1.047.442 du 9 septembre 1957. Comme matières premières, on utilisera aussi les produits que l'on peut obtenir par copolymérisation de l'acide fumarique, de l'anhydride maléique, des semi-esters maléiques, de l'acide crotonique, de l'acide acrylique avec le styrène, l'isobutylène, l'acétate de vinyle, le chlorure de vinyle, le chlorure de vinylidène, le butadiène, l'isoprène ou encore les produits d'addition de 2 moles d'acide oléique sur le m-xylène, les condensats acide salicylique-formaldéhyde, la carboxyméthylcellulose, les copolymérisats d'acide acrylique et d'acide linoléique, les produits d'addition du thioglycol et/ou des acides mercaptocarboxyliques sur des dérivés qui comportent des doubles liaisons, par exemple sur des polymérisats du butadiène ou de l'isoprène ou des copolymérisats de ceux-ci avec les dérivés vinyliques.

Les produits d'éthérification des silanols ou des siloxanes avec des polyesters linéaires ou ramifiés ou des polyéthers ainsi que les polyacétals que l'on peut obtenir par les procédés bien connus, les dérivés

comportant des groupes époxy sont des composants convenables pour la préparation de produits mousse. Les dérivés polycarboxylés doivent être liquides à la température ambiante pour faciliter la fabrication industrielle des produits mousse. Tant que les dérivés polycarboxylés sont fortement visqueux ou solides, il est recommandé de mélanger aussi avec d'autres composants. Dans chaque cas, on doit faire attention à ce qu'il y ait un nombre suffisant de groupes carboxyles. L'indice d'acide doit être supérieur à 20, de préférence on opère avec des indices d'acide de 30-60, mais même des combinaisons avec des indices d'acide supérieurs à 100 peuvent être traitées avec succès.

Les polyisocyanates ou combinaisons de polyisocyanates doivent être également liquides à la température ambiante. On peut mettre en œuvre aussi bien des polyisocyanates simples, tels qu'on les obtient par phosgénation d'amines correspondantes, que des polyisocyanates de poids moléculaire plus élevé que l'on obtient par réaction de dérivés comportant des atomes d'hydrogène réactifs avec un excès de polyisocyanates simples. Les isocyanates convenables sont, par exemple, toluylène-2,4- et toluylène-2,6-diisocyanate, 1-méthyl-3,5-diéthylbenzène-2,4-diisocyanate, m-phénylène-diisocyanate, p-phénylènediisocyanate, diphénylméthane-4,4'-diisocyanate, naphtalène-1,5-diisocyanate, hexaméthylènediisocyanate, 4,4',4'' - triphénylméthane - triisocyanate ou encore l'isocyanate à poids moléculaire élevé obtenu par réaction de 1 mol de triméthylolpropane avec 3 mols de toluylène-diisocyanate ou celui que l'on obtient par réaction d'un polyéther ramifié, préparé à partir de triméthylolpropane et oxyde de propylène avec un excès de toluylène diisocyanate ou encore des isocyanates trimérisés et polymérisés comme ils sont décrits dans le brevet allemand n° 951.168, du 1er février 1953. L'emploi simultané de mono-isocyanates n'est pas exclu, cependant, la proportion doit être maintenue faible, comparée à celle des polyisocyanates. Les polyisocyanates ou mélanges de polyisocyanates peuvent être utilisés, par rapport aux atomes d'hydrogène susceptibles de réagir, en quantités inférieures, en quantités équivalentes ou en excès. L'excès d'isocyanate ne doit pas dépasser le double de la quantité équivalente.

L'emploi simultané d'activateurs est nécessaire. Etant donné que les groupes carboxyliques réagissent plus lentement que les groupes hydroxyles, on utilise la plupart du temps des activateurs très réactifs.

Conviennent particulièrement bien les dérivés organiques ou minéraux, à réaction alcaline en milieu aqueux, ou les dérivés dans lesquels le groupement $-\overline{\underline{O}}^{-}Me^{+}$ est contenu au moins une fois, Me représentant un métal alcalin ou un groupe ammonium quaternaire. On citera les hydroxydes alcalins, les alcoolates ou phénolates alcalins ainsi que les sels alcalins d'acide carboxylique y compris l'acide carbonique. Mais on peut employer aussi des amines tertiaires aliphatiques comme par exemple des alcoylène-polyamines perméthylées du type de la tétraméthyléthylènediamine ou de la diéthylènetriamine perméthylée ainsi que la diméthylpipérazine, l'hexahydrodiméthylaniline, le 1,4-diaza-bicyclo-(2,2,2)-octane. Les dérivés métalliques solubles en milieu organique, comme par exemple dilaurate de dibutylétain, oléate d'étain II, conviennent également en particulier en combinaison avec les activateurs mentionnés. Si l'on met en œuvre les activateurs qui sont en mesure de former des ions hydroxyles ou des ions hydroxyles substitués, on observe que, dans le processus de moussage, il se forme une quantité de gaz carbonique plus grande que dans la réaction des groupes carboxyles avec l'isocyanate avec formation de groupes carbonamides. Cet effet est particulirement visible lors de la mise en œuvre d'un excès d'isocyanate. Ceci est un autre avantage du procédé par rapport aux modes opératoires dans lesquels il n'y a pas de groupes carboxyles présents.

Les hydrocarbures saturés ou non, halogénés, qui sont mélangés avec les réactifs usuels, possèdent un point d'ébullition inférieur à 150 °C. De préférence, on utilise des agents porogènes qui présentent un point d'ébullition inférieur à 50°. On citera par exemple trichlorofluorométhane, dichlorodifluorométhane, chlorodifluorométhane, dichlorofluorométhane, dichlorotétrafluoroéthane, chlorure d'éthyle, 1,1-dichloréthane, 1,1-dichloréthylène, 1,2-dichloréthylène, chlorure de n-propyle, chlorure de n-butyle, trichlorofluoroéthylène, tétrafluoroéthylène, trifluorochloréthylène, 2,2-difluoro-1,1-dichloréthylène, 3,3,3-trifluoropropène. Ces liquides à bas point d'ébullition ou ces gaz liquéfiables peuvent être ajoutés au ou injectés dans le polyisocyanate ou le dérivé polycarboxylique ou bien, dans un mode opératoire automatique, au courant des composants en un point quelconque. L'emploi d'agents porogènes qui dégagent des gaz à température élevée est une autre possibilité de réduire le poids volumique de la mousse. On peut utiliser par exemple l'azodiisobutyronitrile, l'azodicarboxylate d'éthyle, la dinitrosopentaméthylène tétramine.

On peut utiliser, en même temps, également, des colorants comme par exemple des pigments minéraux ou organiques, de la manière bien connue, des charges comme par exemple le noir, le gel de silice, des poudres métalliques. En outre, on peut ajouter au mélange de réactifs capable de mousser des stabilisants de mousse, des tensio-actifs à anions actifs, à cation actif, ou non-ionogènes ainsi que des agents pyropassivants comme le phosphate de trichloréthyle ou le phosphate d'ammonium. Parfois, des additions de plastifiants comme des hydrocarbures

paraffiniques fortement chlorés ou des esters phtaliques apportent des effets particuliers.

On peut conduire le procédé en discontinu ou en continu. Dans ce dernier cas, on utilise des installations telles que celles qui sont décrites dans le brevet français n° 1.074.713 du 9 mai 1957 et dans le brevet des Etats-Unis d'Amérique n° 2.764.565 du 8 août 1955.

Les produits sont des mousses demi-rigides ou rigides, on peut les utiliser pour des constructions en matériau léger ou bien pour des isolations calorifiques, frigorifiques ou phoniques.

Exemple 1. — *a.* On mélange 700 parties d'un produit d'addition d'oxyde de propylène sur le triméthylolpropane présentant un indice d'hydroxyle de 350 avec 300 parties d'acide linoléique dimérisé (indice d'acide 180). L'indice d'acide de ce mélange est de 54. On mélange intensivement ce mélange avec 20 parties de l'éther de propylèneglycol ramifié mentionné ci-dessus, contenant 0,18 partie de sodium fixé sous forme d'alcoolate, 1 partie de diéthylènetriamine perméthylée, 1 partie d'un mélange d'un phénylméthylpolysiloxane linéaire et d'un ramifié avec une solution de 10 parties de trichlorofluorométhane dans 90 parties de toluylènediisocyanate.

Le mélange réactionnel crémeux commence immédiatement à mousser avec une vitesse modérée et se solidifie en une mousse rigide de poids volumique de 25 kg/m^3.

b. On obtient une mousse également rigide, avec un poids volumique de 30 kg/m^3 en mélangeant 100 parties du mélange indiqué ci-dessus, possédant un indice d'acide de 54, avec 2 parties de diéthylènetriamine perméthylée, 1 partie du phénylméthylpolysiloxane ci-dessus et d'un mélange de 70 parties de toluylènediisocyanate et 10 parties de trichlorofluorométhane.

Exemple 2 : Préparation de la matière première. — On chauffe 1 000 parties d'un éther de polypropylèneglycol ramifié obtenu par fixation d'oxyde de propylène sur le triméthylolpropane (indice d'hydroxyle 350) avec 100 parties d'anhydride succinique, pendant 3 heures, à 150°. Le produit de réaction a un indice d'acide de 50,3 et une viscosité de 1 740 cp/25°.

a. On prépare une mousse à partir de ce dérivé polycarboxylé en mélangeant intensivement 100 parties de celui-ci avec 2 parties de diéthylènetriamine perméthylée, une partie du phénylméthylpolysiloxane cité dans l'exemple 1 et un mélange de 10 parties de trichlorofluorométhane dans 80 parties de toluylènediisocyanate. Le mélange commence à mousser et se solidifie en une mousse rigide avec un poids volumique de 35 kg/m^3.

b. On obtient une mousse analogue en faisant réagir, en plus, encore 0,5 partie d'octoate d'étain-II, avec réduction simultanée de la proportion de diéthylènediamine perméthylée de 2 à 1 parties.

Exemple 3. — On mélange 65 parties d'un mélange de 700 parties d'huile de ricin et 300 parties d'acide gras de l'huile de lin dimérisé (indice d'acide du mélange 56, viscosité 1 530 cp/25°) avec 35 parties d'un éther de polypropylèneglycol ramifié, obtenu par fixation d'oxyde de propylène sur le triméthylolpropane (indice d'hydroxyle de 380) contenant 0,4 % de sodium sous forme d'alcoolate, 1 partie du phénylméthylpolysiloxane indiqué dans l'exemple 1 et d'une solution de 10 parties de trichlorofluorométhane dans 75 parties de toluylènediisocyanate. Au cours d'une réaction modérée, il se forme une mousse semi-élastique avec un poids volumique de 43 kg/m^3.

Exemple 4. — On mélange intensivement 100 parties d'un polyester obtenu à partir de 1,75 mol d'acide adipique, 1,75 mol de diéthylèneglycol et 1 mol de glycérine (indice d'acide 30; indice de OH364; viscosité 1 120 cp/25°), avec 2 parties d'une solution de potasse à 17 % dans l'alcool benzylique et l'alcool méthylique (3 : 1), 2 parties de diéthylènetriamine perméthylée et avec une solution de 40 parties de trichlorofluorométhane dans 160 parties de 4,4'-diphénylméthanediisocyanate avec 33 % de NCO. Le mélange réactionnel commence à mousser avec une vitesse modérée et se solidifie en 3 minutes environ pour donner une mousse rigide à pores fins.

Exemple 5. — On mélange 100 parties d'un polyester, obtenu à partir de 5 mols d'acide adipique, 5 mols de triéthylèneglycol et 3,34 mols d'hexanetriol-1,2,6 avec 2 parties d'une solution de potasse à 17 % dans le mélange alcool benzylique et alcool méthylique (3 : 1), 1,5 partie d'hexahydrodiméthylaniline, 1 partie du dérivé silicique indiqué dans l'exemple 1, puis avec des hydrocarbures halogénés en solution dans 150 parties de toluylènediisocyanate comme décrit dans l'exemple 6.

a. 14 parties de 1,1-dichloréthylène.

b. 13,4 parties de chlorure de n-butyle.

c. 16,4 parties de 1,2-dichloropropane.

d. Chlorure de tertiobutyle.

Les mélanges réactionnels commencent immédiatement à mousser et se solidifient, au bout d'un temps court, en des mousses rigides avec une structure de pore régulière. sans coloration du noyau.

Exemple 6. — On mélange intensivement 100 parties en poids d'un polyester obtenu à partir de 1,75 mol d'acide adipique, 175 mol de diéthylèneglycol et 1 mol de glycérine (indice d'acide 30; indice d'hydroxyle 364; viscosité 1 120 cp/25°) avec 2,5 parties d'une solution à 17 % de potasse dans le mélange alcool benzylique-méthanol (3 : 1), 1 partie du phénylméthylpolysiloxane décrit dans l'exemple 1, ainsi qu'un mélange de 10 parties de trichlorofluorométhane dans 150 parties d'un toluylènediisocyanate modifié. Après mélangeage intensif

des composants, la masse se met à mousser immédiatement et se solidifie, au bout d'un temps court, en une mousse résistant au frottement, rigide.

On obtient le toluylène diisocyanate modifié par réaction de 15 parties d'un éther de polypropylèneglycol obtenu par fixation d'oxyde de propylène sur le triméthylolpropane (indice d'hydroxyle 365) avec 85 parties de toluylènediisocyanate. La teneur en NCO s'élève à 33,7 %, la viscosité 94,5 cp/25°.

Exemple 7. — On mélange intensivement 100 parties d'un polyester obtenu à partir de 730 parties d'acide adipique, 636 parties de diéthylèneglycol et 357 parties de triméthylolpropane (indice d'acide 30,5; indice de OH 381; viscosité 919 cp/25°), avec 6 parties d'une solution de potasse à 17 % dans le mélange alcool benzylique et alcool méthylique (3 : 1), 1 partie du dérivé silicique décrit dans l'exemple 1 et une solution de 10 parties de trichlorofluorométhane dans 160 parties de 4,4'-diphénylméthanediisocyanate (33 % de NCO). Le mélange, analogue à de la crème, commence à mousser immédiatement et se solidifie en quelques minutes pour donner une mousse semi-rigide, résistant au frottement, à pores fins, avec une structure de pores fins très régulière. La mousse présente une bonne adhérence exceptionnelle aux parois du récipient. Poids volumique 33 kg/m³.

RÉSUMÉ

L'invention a pour objet un procédé pour la préparation de mousses à base d'isocyanate, à partir de dérivés polycarboxylés avec un poids moléculaire supérieur à 200, des polyisocyanates, des activateurs et des agents porogènes, caractérisé par les points suivants pris isolément ou en combinaison :

1° Les dérivés polycarboxylés avec un indice d'acide supérieur à 20 et un total de l'indice d'acide et de l'indice d'hydroxyle de 150-600, en l'absence d'eau, avec, au maximum, le double de la quantité équivalente de polyisocyanate, en présence d'hydrocarbures halogénés saturés et/ou insaturés présentant un point d'ébullition inférieur à 150;

2° On emploie comme activateurs des dérivés organiques ou minéraux, à réaction alcaline en milieu aqueux, dans lesquels le groupement $\overline{O}^{-}Me^{+}$ est contenu au moins une fois, Me représentant un métal alcalin ou un groupe ammonium quaternaire.

Société dite :
FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT

Par procuration :
G. Beau de Loménie, André Armengaud et G. Houssard

6

PATENT SPECIFICATION

950,876

NO DRAWINGS

950,876

Date of Application and filing Complete Specification: May 1, 1961. No. 15726/61.

Application made in Germany (No. F31174 IVb/39b) on May 6, 1960.

Complete Specification Published: Feb. 26, 1964.

Index at acceptance:—C3 R(32B1, 32B2, 32C1, 32C6, 32C10, 32C12, 32C13, 32D1, 32D2, 32D3, 32D4, 32D6, 32E2, 32G1, 32H1, 32H3, 32H5, 33C1, 33C6, 33C10, 33C12, 33C13, 33G, 33P); C3 C1E2

International Classification:—C 08 g (C 08 j)

COMPLETE SPECIFICATION

Improvements in or relating to the production of Cellular Polyurethane Plastics

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, of Leverkusen-Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for preparing cellular polyurethane plastics.

It is known to produce cellular plastics by the isocyanate-polyaddition process from relatively high molecular weight compounds containing active hydrogen atoms and polyisocyanates. Carbon dioxide is evolved during the course of the reaction and this carbon dioxide blows the structure to form the cellular material. In this process, relatively high molecular weight carboxyl-containing compounds have been employed. When cellular materials are produced on a large industrial scale, the reaction to produce carbon dioxide is accomplished by utilising a compound containing hydroxyl groups and water which reacts with —NCO groups to produce carbon dioxide. This process has the disadvantage of being uneconomical with respect to isocyanate consumption as one mol of water uses up two —NCO groups.

It is also known to produce cellular materials by reacting polyhydroxy compounds with polyisocyanates in the presence of haloalkanes as blowing agents either by themselves or in the presence of water. The cellular materials produced by this process and especially where no water is employed have a higher degree of softness than the materials produced using water as the only blowing agent as described above.

In the latter process, the blowing is effected exclusively by the haloalkanes and the process may be carried out not only in the complete absence of water, but in the absence of carboxyl groups, thereby preventing the formation of carbon dioxide. These processes suffer from the disadvantages that where water is used in combination with a haloalkane, it is necessary to match the reaction of the —NCO to hydroxyl group and the —NCO to water reactions so that they proceed synchronously. This ensures the production of a cellular material. If the reactions are not synchronised, the carbon dioxide produced by the water —NCO reaction will be released either before the reaction mass has reached a viscosity to hold the carbon dioxide in small bubbles or after the viscosity is so great that a non-uniform product is formed. Further, the utilisation of water is not economically feasible for the reason that more expensive isocyanate is required in this reaction.

Where the blowing is caused solely by the use of a haloalkane, only urethane groups are formed as a result of the reaction by the hydroxyl groups and —NCO groups. Therefore, no urea groups which are capable of developing secondary valence bonds are formed. These bonds improve the physical properties of the resulting cellular polyurethane.

According to the present invention there is now provided a process for making cellular polyurethane plastics, which comprises reacting under substantially anhydrous conditions an organic compound containing a plurality of carboxyl groups, having a molecular weight of at least 200 and an acid number of at least 20 with an organic polyisocyanate in the presence of a halohydrocarbon having a boiling point less than 150°C. and a catalyst for the reaction between isocyanate and carboxy groups.

More particularly, the invention resides in the reaction of carboxyl groups with —NCO groups to produce carbon dioxide in combination with the formation of gas by the vaporisation of a halohydrocarbon to produce a cellular polyurethane plastic in the absence of water. By this process, less isocyanate is utilised thus reducing the cost of one of the major constitutents and also removing the need to synchronise the —NCO hydroxyl group and the —NCO water reactions. Further, in the practice of this invention the blowing is effected as a result of the reaction of the —NCO groups with the —COOH groups with the formation of a carbonamide group, carbon dioxide being simultaneously split off. The carbonamide group, like the urea groups formed when using water, are capable of developing secondary valence bonds which improve the properties of the resulting cellular product. The blowing action, of course, is due to the liberation of carbon dioxide and to the vaporisation of the halohydrocarbon.

In the practice of this invention it is essential that the compound containing a plurality of carboxyl groups has an acid number of at least 20 and a molecular weight of at least 200, preferred compounds being those having a molecular weight of from 500 to 2500. These compounds may also contain one or more hydroxyl groups. In this case the sum of the acid number and the hydroxyl number should be from 150 to 600. Any suitable compound containing a plurality of carboxyl groups and having the particular characteristics described above may be used in the process according to the present invention. Suitable compounds are linear and branched polyesters prepared by reacting polyfunctional alcohols, amino alcohols, hydroxycarboxylic acids, aminocarboxylic acids or polycarboxylic acids. By the proper choice of proportions of the reactants and the reaction conditions, it is readily possible to produce polyesters containing either carboxyl groups alone or both carboxyl and hydroxyl groups.

Any suitable polyfunctional alcohol may be used in the preparation of the polyesters containing a plurality of carboxyl groups, for example, ethylene glycol, diethylene glycols of the general formula:

$$HO[—CH_2—CH_2—O]_n—CH_2—CH_2—OH$$

in which n is an integer greater than one, propylene glycol, dipropylene glycol, polypropylene glycols of the general formula:

$$HO\left[\begin{array}{l}CH—CH_2—O\\ |\\ CH_3\end{array}\right]_n\begin{array}{l}CH_2—CH—OH\\ \quad\quad\;\; |\\ \quad\quad\;\; CH_3\end{array}$$

in which n is an integer greater than one, glycols of the general formula:

$$HO—[CH_2—]_nOH$$

in which n is an integer greater than two, butane - 1,3 - diol, butane - 2,3 - diol, dimethyl - 2,2 - propane - 1,3 - diol, 2 - butane-1,3 - butanediol, glycerine, trimethylolpropane, hexane - 1,2,6 - triol, pentaerythritol, sorbitol and addition products of alkylene oxide, for example, ethylene oxide, propylene oxide, 1,2- or 1,3-butylene oxide, styrene oxide, epichlorohydrin and tetrahydrofuran with any of the previously mentioned polyfunctional alcohols. Any suitable polycarboxylic acid may be used in the preparation of the polyesters, for example, tartaric acid, citric acid, oxalic acid, alkylene dicarboxylic acids having the general formula:

$$HOOC[—CH_2—]_n—COOH$$

wherein n is an integer, for example, adipic acid, succinic acid and suberic acid; maleic acid, fumaric acid, phthalic acids, including iso- and terephthalic acids, dimeric polycarboxylic acids and higher functional acids obtained by polymerisation of unsaturated fatty acids, for example, ricinoleic acid and sorbic acid; and polycarboxylic acids obtained by diene synthesis for example, maleic acid anhydride or hydrogenation products thereof.

Polyesteramides are also suitable for employment as the compound containing a plurality of carboxyl groups. Any suitable polyesteramide may be used such as those prepared by admixing amino alcohols, polyamines and/or aminocarboxylic acids in the preparation of any of the polyesters mentioned above to obtain polyesteramides. Any suitable amino alcohol may be used, for example, aminoethyl alcohol, aminopropyl alcohol, aminobutyl alcohol and aminoxylyl alcohol. Any suitable polyamine may be used, for example, ethylene diamine, propylene diamine, butylene diamine, cyclohexylene diamine, xylylene diamine and toluylene diamine. Any suitable aminocarboxylic acid may be used, for example, aminoacetic acid, α-aminopropionic acid, α - aminoisovaleric acid, α-amino - α - methyl butyric acid, α - aminosuccinic acid, α - aminoglutaric acid and α-amino - β - imidazole propionic acid. Polyesteramides containing tertiary nitrogen atoms may also be used.

The polyesters or polyesteramides may also be modified with monofunctional alcohols or polycarboxylic acids for example, with saturated and unsaturated fatty acids including lauric acid, palmitic acid, steric acid and linoleic acid.

Other suitable compounds containing a

plurality of carboxyl groups may be used such as those obtained by the addition of polycarboxylic acid anhydrides to linear or branched components containing hydroxyl groups, for example, hydroxyl polyesters, polyesteramides, polyhydric polyalkylene ethers, polyhydric polythioethers and polyacetals. Any suitable anhydride may be used, for example, the anhydrides of maleic acid, succinic acid, phthalic acid, hexahydrophthalic acid, citraconic acid, pyromellitic acid and trimellitic acid.

Any suitable hydroxyl polyester may be used, for example, those produced by the thermal condensation of a polycarboxylic acid and a polyhydric alcohol. Any suitable polycarboxylic acid may be used, for example, succinic, oxalic, adipic, methyladipic, sebacic, glutaric, pimelic, azelaic and suberic acid; aromatic carboxylic acids including phthalic, terephthalic, isophthalic and 1,2,4 - benzene tricarboxylic acid; sulphur containing acids, for example, thiodiglycollic and thiodipropionic acid; and unsaturated acids, for example, maleic, fumaric, itaconic and citraconic acid. Any suitable polyhydric alcohol may be used, for example, ethylene glycol, diethylene glycol, propylene glycol, 1,3-butylene glycol, 1,6 - hexanediol, trimethylol - propane, pentaerythritol, glycerine and 1,2,6 - hexanetriol.

Any suitable polyhydric polyalkylene ether may be used, for example, the product obtained by polymerising alkylene oxides or the condensation product of an alkylene oxide with a small amount of a compound containing active hydrogen containing groups, for example, water, ethylene glycol, propylene glycol, butylene glycol, amylene glycol, trimethylol - propane, glycerine, pentaerythritol, 1,6 - hexanediol and 1,2,6 - hexanetriol. Any suitable alkylene oxide may be used, for example, ethylene oxide, propylene oxide, butylene oxide and amylene oxide. The polyhydric polyalkylene ethers may be prepared by any known process, for example by the process described in Wurtz in 1859 and in the *Encyclopedia of Chemical Technology,* Volume 7, pages 257—262 published by Interscience Publishers, Inc. (1951).

Any suitable polyhydric polythioether may be used, for example, the reaction product of one of the aforementioned alkylene oxides used in the preparation of polyhydric polyalkylene ethers with a thioether glycol, for example, thiodiglycol, 3,3' - dihydroxypropyl sulphide, 4,4' - dihydroxybutyl sulphide or 1,4 - (β - hydroxy ethyl) phenylene dithioether.

Any suitable polyesteramide may be used, for example, the reaction product of an amine and/or amino alcohol with a carboxylic acid. Any suitable amine may be used, for example, ethylene diamine or propylene diamine. Any suitable amino alcohol may be used, for example, 1 - hydroxy - 2 - aminoethylene. Any suitable polycarboxylic acid may be used, for example, those disclosed above for the preparation of hydroxyl polyesters.

Any suitable polyacetal may be used, for example, the reaction product of an aldehyde and a polyhydric alcohol. Any suitable aldehyde may be used, for example, formaldehyde, paraldehyde and butyraldehyde. Any of the polyhydric alcohols mentioned above in the preparation of the hydroxyl polyesters may be used.

Organic compounds containing a plurality of carboxyl groups of relatively high molecular weight suitable for use in this invention are obtained by the addition of acrylonitrile to polyhydroxy compounds including those mentioned immediately above and also degraded starch and acetyl cellulose, with the subsequent saponification of the adducts. In some cases the acrylonitrile may be directly replaced by acrylic acid.

Polyalkylene glycol ether - polycarboxylic acids obtained by the oxidation of polyalkylene glycol ethers may be employed in the process of this invention as compounds containing a plurality of carboxyl groups. Other suitable polycarboxyl compounds are the products obtained by the copolymerisation of fumaric acid, maleic acid anhydride, maleic acid semi-esters, crotonic acid and acrylic acid with styrene, isobutylene, vinyl acetate, vinyl chloride, vinylidene chloride, butadiene, isoprene and hexachlorocyclopentadiene. Also suitable are the adducts of two mols of oleic acid with *m* - xylene, salicylic acid-formaldehyde condensates, carboxymethyl cellulose, copolymers of acrylic acid and linoleic acid, addition products of thioglycol and/or mercaptocarboxylic acids with compounds containing double bonds for example with polymers of butadiene or isoprene or copolymers of these with other vinyl compounds.

The polycarboxyl compounds employed in the process of this invention should preferably be liquid at room temperature in order to facilitate the mechanical production of these materials. As the polycarboxyl compounds are highly viscous or solid, they should preferably first be mixed with other components. In every case, care should be taken that a sufficient number of carboxyl groups is available. The acid number of the polycarboxyl compound must be at least 20 and preferably from 30 to 60. However, polycarboxyl compounds having acid numbers greater than 100 can be processed with good results.

The polyisocyanates and polyisocyanate combinations should also preferably be liquid at room temperature. Both simple polyisocyanates, such as those obtained directly by the phosgenation of suitable amines, and polyisocyanates of higher molecular weight prepared by reacting a compound containing active hydrogen atoms with an excess of a

simple polyisocyanate can be used. Suitable isocyanates are, *inter alia*, for example, toluylene - 2,4- and toluylene - 2,6 - diisocyanates, 1 - methyl - 3,5 - diethylbenzene-2,4 - diisocyanate, *m* - phenylene diisocyanate, *p* - phenylene diisocyanate, diphenylmethane-4,4[1] - diisocyanate, naphthalene 1,5 - diisocyanate, hexamethylene diisocyanate, 4,4[1],4[11]-triphenylmethane triisocyanate, furfurylidene diisocyanate, the isocyanate of relatively high molecular weight obtained by reacting one mol of trimethylol - propane with three mols of toluylene diisocyanate, the isocyanate obtained by reacting a branched polyether prepared from trimethylol-propane and propylene oxide with an excess of toluylene diisocyanate and trimerised and polymerised isocyanates. Monoisocyanates may be simultaneously employed with the polyisocyanates, provided the proportion of monoisocyanate is kept small. The polyisocyanates and polyisocyanate mixture may be employed in quantities less than, equal to or greater than the equivalent quantity, based on the active hydrogen atoms. However, the isocyanate should not be employed in an amount exceeding twice the equivalent quantity.

The simultaneous use of activators is essential in the process according to the present invention. Preferably very reactive activators are employed since carboxyl groups react more sluggishly than hydroxyl groups. Any suitable activator may be used in the process of this invention, for example, organic and inorganic compounds which show an alkaline reaction in aqueous medium and which contain at least one $—O]^{-}Me^{+}$ groupings, where Me represents an alkali metal or a quaternary ammonium group, tertiary amines and metal compounds which are soluble in organic media. Any suitable compound which shows an alkaline reaction and which contains at least one $—O]^{-}Me^{+}$ group may be used, for example, alkali metal hydroxides, alkali metal alcoholates, alkali metal phenolates and alkali metal salts of carboxylic acids including sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium methylate, sodium ethylate, potassium methylate, lithium ethylate, potassium phenylate, sodium phenylate, sodium acetate, potassium acetate, potassium carbonate, sodium formate and sodium carbonate. Any suitable tertiary amine catalyst may be used, for example, permethylated alkylene polyamines such as tetramethyl ethylene diamine and permethylated diethylene diamine; dimethyl piperazine, hexahydrodimethylaniline and 1,4 - diazabicyclo - (2,2,2)-octane. Any suitable metal compound soluble in organic media may be used such as dibutyl tin dilaurate, tin-II-oleate and any of the organic compounds disclosed in *Journal of Applied Science*, Vol. IV, issue No. 11, pp. 207—211 (1960). Combinations of any of the above activators may also be used. Organic and inorganic compounds which show an alkaline reaction in aqueous media are preferred. When using such activators which are capable of forming hydroxyl ions or substituted hydroxyl ions, a larger quantity of carbon dioxide is formed during the foaming process than is expected from the reaction of the carboxyl groups with the isocyanate groups which form carbonamide groups. This is particularly apparent when an excess of isocyanate is employed. This is a further advantage of the present process over those heretofore known in the art.

Any suitable halogenated saturated or unsaturated hydrocarbon having a boiling point below 150°C. may be used in the process of this invention. Preferred blowing agents are those having a boiling point below 50°C. Suitable blowing agents are trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, dichlorofluoromethane, dichlorotetrafluoroethane, ethyl chloride, 1,1-dichloroethane, 1,1 - dichloroethylene, 1,2-dichloroethylene, *n* - propyl chloride, n-butyl chloride, trichlorofluoroethylene, tetrafluoroethylene, trifluorochloroethylene, 2,2-difluoro - 1,1 - dichloroethylene and 3,3,3 - trifluoropropene. The halogenated hydrocarbons are preferably employed in an amount of from 10 to 50 parts by weight based on the weight of the polycarboxylic acid component and contribute up to 75% of the blowing action and preferably from 30% to 60%.

These low boiling liquid or liquefied gases are admixed with the polyisocyanate or the polycarboxyl compound. When a suitable machine such as that disclosed in British Specification No. 769,682 is used to mix the components, the halogenated hydrocarbons may be introduced or injected into the flowing stream of components at any suitable point.

Blowing agents which split off gases at elevated temperatures may also be simultaneously employed in order to reduce the weight per unit volume of the resulting foam materials. Examples of such blowing agents are azodiisobutyric acid nitrile, azodicarboxylic acid diethyl ester and dinitrosopentamethylenetetramine.

Dyestuffs, such as organic and inorganic pigments, may also be used in known manner in the production of the foam materials, as well as fillers, for example carbon black, silica gel and metal powder. Foam stabilisers, anion-active, cation-active and non-ionic emulsifiers, as well as fire-proofing agents, such as trichloroethyl phosphate and ammonium phosphate may also be added to the foamable reaction mixtures. It is also sometimes advantageous to add a plasticiser, for example a highly chlorinated paraffin hydrocarbon or a phthalic acid ester to the reaction mixture.

The process according to the present inven-

tion may be carried out either batch-wise or continuously. In the latter case, the reaction is carried out in a mechanical device, for example in the apparatus described in British Specification 769,682.

The products obtained by the process according to the present invention are semi-rigid or rigid foam materials and they can be used for the production of laminates of light-wieght materials or for insulation purposes against heat, cold or sound.

In order that the invention may be more clearly understood, the following Examples, in which all parts are by weight unless otherwise stated, are given by way of illustration only:—

EXAMPLE 1.

a) 700 parts of an addition product of propylene oxide with trimethylolpropane and having an hydroxyl number of 350 are mixed with 300 parts of dimerised linseed oil fatty acid having an acid number of 180. The acid number of the resulting mixture is 54. 80 parts of the mixture thus produced are thoroughly mixed with 20 parts of the aforementioned branched polypropylene glycol ether, containing 0.18 part of sodium combined as alcoholate, 1 part of permethylated diethylene triamine, 1 part of a mixture of a linear and a branched phenylmethyl polysiloxane and with a solution of 10 parts of trichlorofluoromethane in 90 parts of toluylene diisocyanate.

The creamy reaction mixture immediately starts to foam at moderate speed and solidifies to form a rigid foam material having a weight per unit volume of 25 kg/m^3.

b) A similar rigid foam material having a weight per unit volume of 30 kg/m^3 is obtained if 100 parts of the aforementioned mixture having an acid number of 54 are mixed with 2 parts of permethylated diethylene triamine, 1 part of the aforementioned phenylmethyl polysiloxane and with a mixture of 70 parts of toluylene diisocyanate and 10 parts of trichlorofluoromethane.

EXAMPLE 2.

Production of the starting material:

1,000 parts of a branched polypropylene glycol ether having an hydroxyl number of 350 and which had been prepared by adding propylene oxide to trimethylolpropane are heated with 100 parts of succinic acid anhydride at 150°C. for 3 hours. The reaction product has an acid number of 50.3 and a viscosity of 1740 cP/25°C.

a) 100 parts of the polycarboxyl compound thus prepared are thoroughly mixed with 2 parts of permethylated diethylenetriamine, 1 part of the phenylmethyl polysiloxane employed in Example 1 and with a mixture of 10 parts of trichlorofluoromethane in 80 parts of toluylene diisocyanate. The resulting mixture starts to foam and solidifies into a rigid foam material having a weight per unit volume of 35 kg/m^3.

b) A similar foam material is obtained if there is additionally used 0.5 part of tin-II-octoate, while simultaneously reducing the proportion of permethylated diethylene triamine from 2 parts to 1 part.

EXAMPLE 3.

65 parts of a mixture of 700 parts of castor oil and 300 parts of dimerised linseed oil fatty acid (acid number of the mixture 56, viscosity 1530 cP/25°C.) are thoroughly mixed with 35 parts of a branched polypropylene glycol ether having an hydroxyl number of 380 prepared by adding propylene oxide to trimethylolpropane, and containing 0.4% of sodium combined as alcoholate, 1 part of the phenylmethyl polysiloxane employed in Example 1 and with a solution of 10 parts of trichlorofluoromethane in 75 parts of toluylene diisocyanate. A semi-elastic foam material having a weight per unit volume of 43 kg/m^3 is formed in a moderate reaction.

EXAMPLE 4.

100 parts of a polyester having an acid number of 30, an hydroxyl number of 364 and a viscosity of 1120 cP/25°C. obtained from 1.75 mols of adipic acid, 1.75 mols of diethylene glycol and 1 mol of glycerine are mixed, while stirring vigorously, with 2 parts of a 17% potassium hydroxide solution in benzyl alcohol and methyl alcohol (3:1), 2 parts of permethylated diethylenetriamine and a solution of 40 parts of trichlorofluoromethane in 160 parts of 4,4^1 - diphenylmethane diisocyanate containing 33% NCO. The reaction mixture starts to foam at moderate speed and solidifies within a period of 3 minutes to form a fine-pored rigid foam material.

EXAMPLE 5.

100 parts of a polyester produced from 5 mols of adipic acid, 5 mols of triethylene glycol and 3.34 mols of hexane - 1,2,6 - triol, having an acid number of 208 and an OH number of 348 are mixed with 2 parts of a 17% potassium hydroxide solution in benzyl alcohol and methyl alcohol (3:1), 1.5 parts of hexahydrodimethylaniline, 1 part of the silicon compound employed in Example 1 and then with solutions of the following halogenated hydrocarbons in 150 parts of modified toluylene diisocyanate as described in Example 6.

a) 14 parts of 1,1-dichloroethylene,
b) 13.4 parts of n-butylchloride,
c) 16.4 parts of 1,2-dichloropropane,
d) 13.4 parts of tertiary-butyl chloride.

The reaction mixtures immediately start to foam and solidify within a short time into rigid foam materials having a regular pore structure and without any discolouration of the core.

Example 6.

100 parts by weight of a polyester having an acid number of 30, an hydroxyl number of 364 and a viscosity of 1120 cP/25°C. formed from 1.75 mols of adipic acid, 1.75 mols of diethylene glycol and 1 mol of glycerine are mixed with 2.5 parts of a 17% solution of potassium hydroxide in benzyl alcohol and methanol (3:1), 1 part of the phenylmethyl siloxane employed in Example 1 and with a mixture of 10 parts of trichlorofluoromethane in 150 parts of a modified toluylene diisocyanate. Afetr thorough mixing of the components, the mass immediately starts to foam and solidifies within a short time to form a rigid, abrasion-resistant foam material.

The modified toluylene diisocyanate is obtained by reacting 15 parts of a polypropylene glycol ether having an hydroxyl number of 365 obtained by adding propylene oxide to trimethylolpropane with 85 parts of toluylene diisocyanate. The NCO content of the modified toluylene diisocyanate is 33.7% and the viscosity 94.5 cP/25°C.

Example 7.

100 parts of a polyester having an acid number of 30.5, an hydroxyl number of 381 and a viscosity of 919 cP/25°C. prepared from 730 parts of adipic acid, 636 parts of diethylene glycol and 357 parts of trimethylolpropane are thoroughly mixed with 6 parts of a 17% potassium hydroxide solution in benzyl alcohol and methyl alcohol (3:1), 1 part of the silicon compound employed in Example 1 and with a solution of 10 parts of trichlorofluoromethane in 160 parts of 4,4'-diphenylmethane diisocyanate (33% NCO). The creamy mixture of the components immediately starts to foam and solidifies within a period of a few minutes to give a fine-pored, abrasion-resistant, semi-rigid foam material having a very uniform and fine pore structure. The foam material thus produced shows an unusually good adhesion to the walls of vessels. Weight per unit volume: 33 kg/m³.

WHAT WE CLAIM IS:—

1. A process for making cellular polyurethane plastics, which comprises reacting under substantially anhydrous conditions an organic compound containing a plurality of carboxyl groups, having a molecular weight of at least 200 and an acid number of at least 20 with an organic polyisocyanate in the presence of a halohydrocarbon having a boiling point less than 150°C. and a catalyst for the reaction between isocyanate and carboxy groups.

2. A process as claimed in claim 1, wherein the organic compound containing a plurality of carboxyl groups also contains one or more hydroxyl groups and the sum of the acid number and the hydroxyl number is from 150 to 600.

3. A process as claimed in claim 1 or claim 2, wherein the acid number of the organic compound containing a plurality of carboxyl groups is from 30 to 60.

4. A process as claimed in any of the preceding claims, wherein the halohydrocarbon has a boiling point of less than 50°C.

5. A process as claimed in any of the preceding claims, wherein the organic compound containing a plurality of carboxyl groups has a molecular weight of from 500 to 2500.

6. A process as claimed in any of the preceding claims, wherein the halohydrocarbon is employed in an amount of from 10 to 50 parts by weight, based on the weight of the organic compound containing a plurality of carboxyl groups.

7. A process for making cellular polyurethane plastics, substantially as described with reference to any of the Examples.

8. Cellular polyurethane plastics, when prepared by the process claimed in any of the preceding claims.

ELKINGTON & FIFE,
Chartered Patent Agents,
Bank Chambers, 329, High Holborn,
London, W.C.1.
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.